Nanoscale Science and Engineering Center

Science of Nanoscale Systems and their Device Applications

Harvard, MIT, UC Santa Barbara, and Museum of Science, Boston



Annual Report 2008–2009

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3. PROJECT SUMMARY

Our Center develops tools to study nanoscale systems. We would like to control electrons and photons inside nanostructures for new nanoelectronic and nanophotonic devices, and to investigate how biological systems function at the nanoscale using techniques from the Physical Sciences. Three Research Clusters address these goals:

Cluster 1: Tools for Integrated Nanobiology builds bridges between the Physical Sciences, Biology and Medicine. Powerful new tools for manipulating and testing biological cells and tissues can be made using microfluidic systems, soft lithography, and semiconductor technology. Biology and Medicine offer an enormous range of engaging problems in functional biological systems, and the opportunity to think about "hybrid" systems that combine biological and non-biological components.

Cluster 2: Nanoscale Building Blocks makes new classes of nanostructures that exhibit size-dependent properties. We synthesize structures with unconventional shapes, as well as zero, one- and two-dimensional nanostructures including nanoparticles, nanowires, and heterostructures. New materials are introduced, including oxide semiconductors and metal chalcogenides. These nanoscale building blocks are promising for nanoelectronics and nanophotonics as well as for biosensors.

Cluster 3: Imaging at the Nanoscale explores new ways to image the quantum behavior of electrons and photons inside nanostructures using custom-made scanning probe microscopes, including cooled instruments. Imaging is an essential tool for the development of nanoelectronics, nanophotonics, and qubits for quantum information processing.

The Center for Nanoscale Systems (CNS) is a major investment by Harvard to provide shared facilities to conduct research in nanoscience and engineering. A new building, the Laboratory for Integrated Science and Engineering has been completed and outfitted with equipment. It houses CNS facilities for nanofabrication, imaging and materials growth. Harvard and UC Santa Barbara provide nanofabrication facilities to outside users through the National Nanotechnology Infrastructure Network (NNIN).

Connections with **Industry** are strengthened by Harvard's **Office of Technology Development** and by the **Industrial Outreach Program**. Our Center is funded by the **Nanoelectronics Research Initiative (NRI)** of the **Semiconductor Research Corporation (SRC)** to develop new oxide materials for future logic switches. Many Center participants have collaborations with industry.

Our Center's **educational program** develops **human resources** at the pre-college, undergraduate, graduate, and postdoctoral levels through a range of activities, including REU and RET programs, a introductory course *Applied Physics 298r* on nanoscience, and a series of workshops. The **Museum of Science**, **Boston** engages the public and introduces them to the big ideas in nanoscience in an entertaining and informative way, in collaboration with the researcher in our Center. The Museum is a core member of the new **National Informal Science Education (NISE) Network**.

Our Center plans to increase **Diversity** by: recruiting a more diverse group of graduate students and postdocs, increasing the diversity of participating faculty, recruiting members of underrepresented groups by extending REU approaches, introducing public school students to science and engineering, and developing long-term partnerships with predominantly female and minority-serving institutions.

4. LIST OF CENTER PARTICIPANTS AND ADVISORY BOARD

(a) Center Participants

Name	Field of Research	Institution
Joanna Aizenberg	Chemical Biology, Materials	Harvard
Carol Lynn Alpert	Education and Outreach	Museum of Science
Raymond Ashoori	Physics	MIT
Michael Aziz	Physics & Applied Physics	Harvard
Moungi G. Bawendi	Chemistry	MIT
Federico Capasso	Applied Physics & Elect. Eng.	Harvard
Kenneth B. Crozier	Electrical Engineering	Harvard
Eugene Demler	Physics Physics	Harvard
Daniel Fisher	Physics	Harvard
Cynthia M. Friend	Chemistry & Applied Physics	Harvard
Gerald Gabrielse	Physics	Harvard
Arthur C. Gossard	Materials	UCSB
Bertrand I. Halperin	Physics	Harvard
Donhee Ham	Electrical Engineering	Harvard
Eric J. Heller	Chemistry & Physics	Harvard
Jennifer E. Hoffman	Physics Physics	Harvard
Marc A. Kastner	Physics	MIT
Efthimios Kaxiras	Physics & Applied Physics	Harvard
Charles M. Lieber	Chemistry & Applied Physics	Harvard
Marko Lonçar	Physics	Harvard
Mikhail Lukin	Physics	Harvard
Charles M. Marcus	Physics	Harvard
Eric Mazur	Applied Physics & Physics	Harvard
Joseph Mizgerd	Biology & Public Health	Harvard
Venkatesh Narayanamurti	Applied Physics & Physics	Harvard
Hongkun Park	Chemistry	Harvard
Mara Prentiss	Physics	Harvard
Kevin (Kit) Parker	Bioengineering	Harvard
Pierre Petroff	Materials	UCSB
Shriram Ramanathan	Materials	Harvard
Howard A. Stone	Materials & Fluid Mechanics	Harvard
Michael Stopa	Computational Materials	Harvard
Michael Tinkham	Physics	Harvard
David Weitz	Materials	Harvard
Robert M. Westervelt	Applied Physics & Physics	Harvard
George M. Whitesides	Chemistry	Harvard
Amir Yacoby	Physics	Harvard
Xiaowei Zhuang	Chemistry & Physics	Harvard
	- •	

International Collaborators

Fabio Beltram	Physics	NEST, Pisa, Italy
Piotr Garstecki	Chemistry	Polish Academy of Sciences
Leo Kouwenhoven	Physics	Delft University of Technology
Eugenia Kumacheva	Chemistry	University of Toronto
Daniel Loss	Physics	University of Basel, Switzerland
Maria-Anita Rampi	Chemistry	University of Ferrara, Italy
Lars Samuelson	Physics	Lund University, Sweden
Hiroyuki Sakaki	Inst. of Industrial Science	University of Tokyo, Japan
Seigo Tarucha	Physics	University of Tokyo and NTT, Japan

Domestic Collaborators

Sangeeta Bhatia Medical Physics Harvard-MIT Health Sci. & Tech.

Donald Eigler Physics IBM, Almaden

Giannoula Klement Biomedicine Children's Hospital, Boston
Dale Larson Biophysics Harvard Medical School
Chinh Pham NanoTech & Business Forum Greenberg Traurig, LLP

Richard Rogers Bioimaging Harvard School of Public Health

National Laboratories

Draper Laboratory Lincoln Laboratory

Oak Ridge National Laboratory

Sandia National Laboratory, Center Integrated NanoTechnologies (CINT)

Public Outreach and Education

Carol Lynn Alpert Museum of Science, Boston Tim Miller Museum of Science, Boston

Robert Graham Harvard Kathryn Hollar Harvard

(b) Members of the External Advisory Board

Kenneth Babcock Si Biosensors George I. Bourianoff Intel Corporation

Donald Eigler IBM, Almaden Research Center

Steven Girvin Yale University
Rachel Goldman University of Michigan

Harald Hess Howard Hughes Medical Institute

Paul L. McEuen Cornell University
Carmichael Roberts WMR Biomedical, Inc.
John Rogers University of Illinois
Richard Slusher Lucent Technologies

Tom Theis IBM, T.J. Watson Research Center

Ellen D. Williams University of Maryland

(c) Academic Participating Institutions

1. Domestic

Boston College

California Institute of Technology

CCNE (MIT, MGH, Harvard Medical School)

Florida State University Georgia Technical Institute Harvard Medical School Harvard School of Public H

Harvard School of Public Health Harvard University NSEC Prime

Harvard University [Center for Nanoscale Systems (CNS); Faculty of Arts and Scienes

(FAS); School of Engineering and Applied Sciences (SEAS)]

Massachusetts Institute of Technology

Nanoscale Informal Science Education (NISE) Network of Museums

National Nanotechnology Infrastructure Network/Harvard

Northeastern University Pennsylvania State University

Princeton University

Stanford University

Texas A&M

Tufts University

Tulane University

University of Arkansas

University of California, Davis

University of California, Los Angeles

University of California, Santa Barbara

University of California, Santa Cruz

University of Illinois, Urbana-Champaign

University of Iowa

University of Maryland

University of New Mexico

University of Oregon

University of Texas, Austin

University of Washington

University of Wisconsin, Madison

Worcester Polytechnic Institute (WPI)

Yale University

2. International

Aston University, UK

Augsburg University, Germany

Bremen University, Germany

Delft University of Technology, The Netherlands

ESPCI, Paris, France

ETH Zürich, Switzerland

Heriot Watt University, UK

Keio University, Japan

Koc University, Istanbul, Turkey

Ludwig Maximilians University, Munich, Germany

Luft University, Sweden

Lund University, Sweden

National Taiwan University

Oldenburg University, Germany

State University of New York-Albary

Technical University of Denmark, Denmark

Technion, Haifa, Israel

Universidad de la Laguna, Tenerife, Spain

University of Basel, Switzerland

University of Bern, Switzerland

University of British Columbia, Canada

University of Ferrara, Italy

University of Linkoping, Sweden

University of Marseille,

University of Montpellier,

University of Paris, France

University of Regensburg, Germany

University of Tokyo, Japan

University of Toronto, Canada

University of Twente, Germany

Weizmann Institute of Science, Rehovot, Israel

(d) Non-academic Participating Institutions

1. Domestic

Advanced Energy Consortium

Agilent Technologies

Alcatel-Lucent, Bell Labs.

AMD

American Chemical Society Petroleum Research Fund

BAE Systems

BSST Industries, LLC, Irwindale, California

CINT/Sandia National Laboratory

Davis Foundation

Draper Laboratory

Eni S.p.A.

GlaxoSmithKline

Grace Construction Products

HRL Laboratories, Malibu, California

Human Frontiers Science Program

IBM Almaden

Intel

Liminus, Inc.

Lincoln Laboratory

Massachusetts General Hospital

Micron

Microsoft Corporation

Museum of Science, Boston

Nanoscale Informal Science Education Network (NISE) Network of Museums

NanoQuine

National Magnet Laboratory

New England Cable News Network

Northrup-Grumman

Oak Ridge National Laboratory

Pranalytica, Inc., Los Angeles

Q-Peak, Inc.

Sandia National Laboratories

Sharp Laboratories of America, Inc.

Schlumberger Doll Research Center, Boston

SRC

Texas Instruments

Unilever, Trumble, CT

Vertex Pharmaceutical

Zena Technologies

2. International

Hamamatsu Photonics, Japan

Institute for High Performance Computing, Singapore

Japan Science and Technology Agency (JST)

Max Planck Institute, Munich, Germany

Max Planck Institute fuer Kohlenforschung, Germany

NanoQuine, Japan

Philips Research, The Netherlands

Riken, Japan

Saint Gobain Research, Paris, France

US-Israel Bi-National Science Foundation

5. MISSION AND BROADER IMPACT

In the following mission statement, taken from our **Project Summary**, we present the goal of our Center — to develop tools for the study of nanoscale systems — and describe its research, education and outreach programs. The **Strategic Research Plan** presented in Section 8 describes how the three Research Clusters below address important applications, and how our investigators work together to reach these goals.

5a. Mission Statement

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5b. Advances in Fundamental Knowledge and Technology

Cluster 1: Tools for Integrated Nanobiology

This Cluster uses technology from the hard sciences to develop tools for Nanobiology. We feature a gold nanowire plasmonic resonator by Whitesides and Capasso.

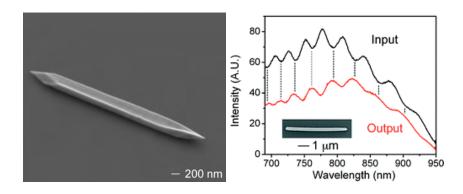


Figure 5.1. Image of a single crystalline gold nanowire (*left*) and spectra at the input and output ends of a nanowire illuminated by near IR radiation (*right*).

Single-Crystalline Metallic Nanowires for Plasmonics

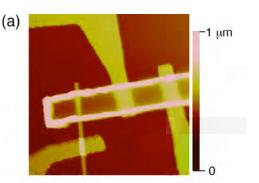
Whitesides and Capasso showed that sectioning of chemically synthesized, single-crystalline microplates of gold with an ultramicrotome (nanoskiving) can be used to produce single-crystalline nanowires (see inset of Fig. 5.1); these nanowires act as low-loss surface plasmon resonators. The diamond knife in the ultramicrotome cuts cleanly through gold microplates that are 35 µm in diameter and 100 nm thick without bending the resulting nanowire, and cuts through the sharp edges of a crystal without deformation to generate nanoscale tips. Figure 5.1 demonstrates how near infrared radiation is guided along a gold nanowire [Wiley *et al.*, Nano Lett. **8**, 3028 (2008)].

Cluster 2: Nanoscale Building Blocks

This cluster synthesizes nanoscale building blocks of different geometries from new materials, and finds ways to couple them to the outside world. We feature new results from Park on hybrid photovoltaic devices, and a new growth facility at UC Santa Barbara.

Nanowire-Polymer Photovoltaic Devices

Hybrid photovoltaic devices, composed of low-cost and solution-processable materials such as conjugated polymers semiconductor nanocrystals, could provide an inexpensive alternative to conventional solar cells. Park has characterized the photovoltaic effect of p-n junctions that consist of a single [poly-3-hexylthiophene (P3HT)] polymer strip and a single CdS nanowires (NW). Spatially resolved photocurrent imaging measurements shown in Figure 5.2 reveal that the zero-bias photocurrent is observed only when the polymer/nanowire interface is illuminated. Estimates of the intrinsic charge separation efficiency for these devices are as high as 40% under laser irradiation with a wavelength of 532 nm. While these results are promising, the study suggests that better interfacial engineering between the two components is



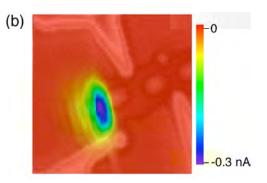


Figure 5.2. (a) AFM image of a heterojunction p-n junction device consisting of a P3HT polymer strip and a single CdS nanowire. The image is 7×7 μ m. (b) Overlap of the simultaneously taken reflection and photocurrent images of the same device.

critical to realizing high-efficiency hybrid solar-cell devices.

New in-situ Growth and Characterization System at UC Santa Barbara

An impressive new growth and characterization system has been installed at UC Santa Barbara in connection with the appointment of <u>Chris Palmstrom</u>. The system, shown above, includes 5 interconnected MBE/CBE systems to grow III-V materials, metals and oxides, allowing new nanocomposites including rare-earth-V and transition metal-V and transition metal-II compounds. Determination of the structure and chemistry at the atomic level at different stages of growth will be done by STM/AFM, Auger, XPS, LEED and RHEED systems. This facility will open many new opportunities for the growth of new types of nanoelectronic, spintronic and photonic structures.

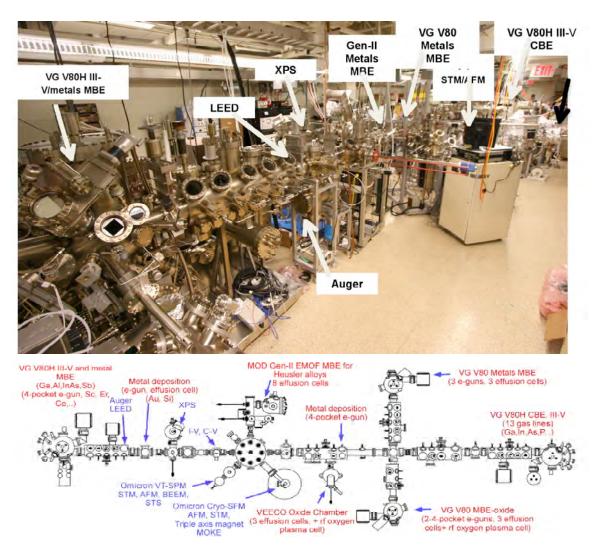


Figure 5.3. New *in-situ* growth and characterization system at UC Santa Barbara.

Cluster 3: Imaging at the Nanoscale

This cluster develops custom-made scanning probe microscopes, and new imaging techniques to visualize electrons and photons inside nanoscale systems. We feature recent achievements by <u>Heller</u> and <u>Hoffman</u>.

Thermal Wavepacket Approach to Semiconductor Transport

Heller has developed a new technique for simulating the flow of electron waves through a nanoscale structure that includes the effect of temperature. By launching wave packets the size of the thermal length, a thermally averaged transport calculation can be performed in one shot including the presence of gate potentials, magnetic fields, random impurities, donor atom fluctuations, etc. This new theoretical tool is very useful for the

analysis of SPM imaging experiments by Westervelt, and it has been successfully applied to a wide range of problems, including transconductance in a 2DEG and a new approach to the Integer Quantum Hall Effect.

High Resolution Magnetic Force Microscope

Jennifer Hoffman is constructing a new cooled force microscope employing a vertical cantilever and a novel AC magnetometry technique with

planned sub-pN sensitivity and sub-nm spatial resolution. She plans to use this instrument to obtain high-resolution images to understand the behavior of superconductors, multi-ferroics, and magnetic nanoparticles. Figure 5.5 shows a photo of the fully assembled microscope system.

5c. Advances in Education

Education is an essential part of our Center. <u>Kathryn Hollar</u> has done an outstanding job organizing our Center's activities in education, outreach and diversity. A description is presented below in Section 5.6e.

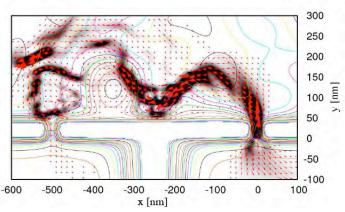


Figure 5.4. Simulations of the flow of electron waves at a finite temperature through a two-dimensional electron gas inside a magnetic focusing device, consisting of two QPCs and a reflecting wall.

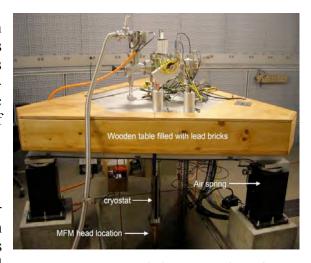


Figure 5.5 Cooled magnetic force microscope with planned sub-pN sensitivity and sub-nm spatial resolution.

The Museum of Science, Boston is a core member of the Nanoscale Informal Science Education (NISE) Network which links together museums and research institutions across the US. Carol Lynn Alpert and Larry Bell are co-PI's of the NISE Network at the Museum of Science. Our NSEC has collaborated with Carol Lynn Alpert since 2001 to bring ideas from nanoscience to the public in an engaging and enjoyable way. The NISE Network allows us to reach a nation-wide audience through entertaining presentations and informative exhibits. The Scientific Advisory Board of the NISE Network includes Eric Mazur, George Whitesides, and Robert Westervelt who are member of our NSEC. We look forward to working closely with the NISE Network to bring the excitement of nanoscience to the public.

The Harvard course *Applied Physics 298r* is run every other year by our NSEC. The course provides an introduction in nanoscience and engineering to undergraduates and graduate students through a series of tutorial lectures by Center faculty about their field

of research, following an overview by the director. The lecture slides are available on the course's website along with an audio recording of each lecture. AP298r is being held in Spring 2009. It gets excellent reviews.

Section 9 *Center Diversity*, Section 10 *Education*, and Section 11 *Outreach*, present the Center's programs in these areas.

5d. Advances in Industrial Collaborations

Harvard is building the connections between academic research with industry. The University created the **Office of Technology Development** (OTD) led by <u>Isaac Kohlberg</u>. Their goals are to manage our intellectual property, and to transition new technologies from scientific research to industry. The Office conducts a broad range of activities ranging from patent applications, to helping faculty connect with industrial executives. OTD director <u>Daniel Behr</u> has become quite familiar with the research of our investigators, and connects with potential industrial applications. Senior executives from major companies have visited Harvard to learn about new research and possible collaborations, an approach that promises to be quite effective.

Our Center was awarded a supplement from the **Nanoelectronic Research Initiative** (**NRI**) of the **Semiconductor Research Corporation** (**SRC**). The semiconductor industry recognizes that technology beyond CMOS will be needed for logic switches in the future, and it is supporting research at universities to help discover the right approach. Our Center is closely related to industry goals, with our emphasis on nanowire devices, nanoelectronics and nanophotonics. The supplement supports <u>Ramanathan's</u> work on switches made from oxide materials.

The Center's international *Frontiers in Nanoscale Science and Technology (FNST)* workshops focus on nanoelectronics, nanophotonics, and quantum information processing:

The 2008 FNST Workshop was held at the University of Basel in January, and included talks on nanoelectronics, nanophotonics, and quantum information processing by an outstanding group including Tony Legget (UIUC), <u>Charles Marcus</u> (Harvard), David DiVincenzo (IBM), Bill Brinkman (Princeton), <u>Seigo Tarucha</u> (Univ. Tokyo), <u>Lars Samuelson</u> (Lund), <u>Amir Yacoby</u> (Harvard), Philip Kim (Columbia), Allan MacDonald (UT Austin), Bart van Wees (Groningen), Atac Imamaglu (ETH Zurich), and <u>Mike Stopa</u> (Harvard).

The 2009 FNST Workshop will be held at Harvard on May 29–31. We will hear talks by an impressive group of speakers from Japan, Europe and the US including: Yasuhiko Arakawa (Univ Tokyo), Phaedon Avouris (IBM), David Awschalom (UCSB), Marija Drndic (Univ. Pennsylvania), Gary Harris (Howard Univ.), Evelyn Hu (Harvard), Koji Ishibashi (RIKEN), Klaus Kern (MPI Stuttgart), Michal Lipson (Cornell), Hideo Ohno (Tohoku Univ.), Chris Palmstrom (UCSB), Pierre Petroff (UCSB), Frances Ross (IBM), Lars Samuelson (Lund Univ.), Seigo Tarucha (Univ. of Tokyo), Jelena Vuckovic (Stanford) and Hiroshi Yamaguchi (NTT Basic Research).

The *Frontiers in Nanoscale Science and Technology Workshops* have proven to be a very effective way for investigators from industry and academia to discuss the future of nanoelectronics and nanophotonics. We look forward to expanding our interactions with NRI and the semiconductor industry in the future.

5e. Current and Potential Impact of NSEC on Education, Workforce Development, Diversity, and Society

The NSEC based at Harvard University has a wide repertoire of activities that contribute to the public understanding of nanoscale science and engineering, encourage participation of underrepresented groups at all levels of education, enhance the infrastructure of research and education at all education levels both locally and internationally.

The collaboration between the NSEC based at Harvard and the Museum of Science, Boston, has been a model for interaction between an informal science organization and a research and higher education organization. This relationship has informed thousands of people of the risks and benefits of nanoscale science and engineering to society through multimedia, television, museum visits, and public presentations; it has also helped practicing scientists and engineers to engage the public in discussions of the *realistic* risks and benefits of this new technology. Participation in the NISE-Network will not only deepen this level of understanding by researchers of how to effectively listen and respond to public concerns regarding nanoscale science and engineering research, it will also allow us to disseminate these new communication models across a wide network of collaborators.

Through our long-standing relationship with the Cambridge Public Schools, a school system with a minority majority population, we introduce over 300 7th grade students each year to scientific research being conducted at Harvard University. Community activities with Cambridge Public Schools impacted another 250 students and their families. The Research Experiences for Teachers program allows us to develop sustained and close relationships with teachers in the Cambridge Public Schools and surrounding school systems. Modules developed through the RET program have been disseminated to over 150 teachers through teacher workshops. As we continue to develop new modules through the RET program, we expect to impact a wider audience through continued dissemination locally and nationally. In all our K12 outreach efforts, we strive to partner with school systems and programs that have a significant population of underserved students.

The REU program is one of our flagship programs for preparing a diverse pool of future leaders in science and engineering. Through aggressive recruiting efforts, 30–40% of our participants each year are from underrepresented groups. Through professional development activities such as presentation and writing skills and mentor training, we not only prepare the participants and mentors scientifically, but help them develop skills that will enhance their careers in science and engineering.

Last year, local and international workshops and collaborations have brought together over 500 practicing scientists, engineers, as well as leaders in business and government, to discuss new directions in nanoscale science and engineering. For example, the

Frontiers in Nanoscale Science and Engineering workshop and Industry Partnership Program at Harvard are annual events that continue to provide opportunities for our faculty, graduate students and postdoctoral researchers to share research results with a wide array of institutions.

6. HIGHLIGHTS

Facilities

LISE & CNS — Harvard University NNIN — Harvard University and University of California, Santa Barbara

Education and Outreach

DragonflyTV Nano — Museum of Science Boston

NanoDays 2008: March 29-April 5 — Museum of Science, Boston

Talking Nano, a 6 DVD Video Set — Museum of Science, Boston

Miniaturizing Assays: Adapting Paper Diagnostics for the K-12 Classroom

Research Cluster 1

Single-Crystalline Gold Nanowires that Guide Light at the Nanoscale — **George M.** Whitesides

CMOS NMR RF Biomolecular Sensor, 1ST Prototype Image — **Donhee Ham** CMOS NMR RF Biomolecular Sensor, 2nd Prototype Image — **Donhee Ham**

CMOS NMR RF Biomolecular Sensor, 3rd Prototype Image — **Donhee Ham**

Anisotrropic Conduction in Engineered Myocardium — Kevin (Kit) Parker

Shear-induced ATP Release from Red Blood Cells — Howard A. Stone

First-Principles Simulation of Electron Injection in Photovoltaic Devices —

Efthimios Kaxiras

Research Cluster 2

SEM, AFM, Reflectance, and Photocurrent Images of a Single CdS-NW-P3HT

Heterojuction — Hongkun Park

Design and Synthesis of Fluorescent-Magnetic Nanoparticle Heterostructures— Moungi Bawendi

Controlling Cellular Morphology and Assembly Using Engineered Nanostructured Substrates — Joanna Aizenberg

Semiconductor Nanowire Lasers — Federico Capasso

A Tunable Quantum Post Terahertz Absorber—Pierre Petroff

Spring Constant Modulation of a Microfabricated Optical Tweezer — Kenneth B. Crozier

Fabricating Novel Nonlinear Optical Platforms — Eric Mazur

Imaging and Atomistic Modeling of Defects on Surfaces: Cl on Au(111)—Cynthia M. Friend

New in situ Growth and Characterization System at UCSB (1) — Arthur Gossard

New in situ Growth and Characterization System at UCSB (2) — Arthur Gossard

Research Cluster 3

Wave-Packet Approach to Semiconductor Transport —Eric J. Heller

High Resolution Force Microscope — Jennifer Hoffman

Imaging and Manipulating Electrons in a One-dimensional Quantum Dot with Coulomb Blockade Microscopy — Bertrand I. Halperin

Measured Spectrum of Localized States in Graphene — Amir Yacoby

Ultra-Low Field Magnetic Resonance Imaging of Hyperpolarized Nuclei — Charles

M. Marcus

Exciton Transfer via Förster — Michael Stopa

Laboratory for Integrated Science and Engineering & Center for Nanoscale Systems Harvard University



Goals

To provide world-class, centralized facilities and technical support for Harvard faculty research groups as well as the larger community of external users from academia and industry.

To foster leading-edge, multi-disciplinary research and education in the area of imaging and nanoscale systems, bridging the disciplines of chemistry, physics, engineering, materials science, geology, biology, and medicine.

To create an environment for collaborative research by providing shared research facilities and meeting places conducive to productive scientific interactions.

National Nanostructure Infrastructure Network (NNIN)

Harvard University and University of California at Santa Barbara



Harvard and UC Santa Barbara are two of an integrated partnership of fourteen user facilities led by Cornell and Stanford that provide opportunities for nanoscience and nanotechnology research. At Harvard, the NNIN provides expertise in computation and in soft lithography and assembly through the Center for Nanoscale Systems. At UCSB, the NNIN provides expertise in optics and electronic materials. The NNIN was funded by the NSF in January 2004.

DragonflyTV Nano Museum of Science, Boston

Dragonfly TV Nano teen actors Jasmine and Ebony Hollis suit up for a clean room visit at Harvard's LISE laboratories.





Dragonfly TV Nano teen actors Jasmine and Ebony Hollis speak with Dave Isadore at Harvard in a scene from the episode on size and scale.

In the spring of 2008, Twin-Cities Public Television filmed scenes at Harvard's NSEC laboratories and at the Museum of Science for two episodes of the PBS kid's series *Dragonfly TV Nano*. The filming was arranged through a partnership between TPT and MOS. Each *Dragonfly TV* episode is viewed by over a million people.

NanoDays 2008: March 29 – April 5 Museum of Science, Boston

Harvard NSEC-associated researchers and graduate students gave talks and demonstrations during the first annual NanoDays event at the Museum of Science. Hundreds of families got to explore the nano world and to see *The Amazing Nano Brothers Juggling Show*.



NanoDays 2008 at MOS: Don Eigler shows youngsters how to move an atom in California through the IBM "Atom-o-Scope" web interface for a scanning probe microscope. Don's talk at MOS was filmed and is included in the *Talking Nano* DVD set. "After watching this DVD, one comes away feeling that one has "seen" the nanoworld," wrote Sir Harry Kroto in his review in *Materials Today*.



The Amazing Nano Brothers Juggling Show features performers Dan Foley and Joel Harris. In this scene, the rings and clubs represent the zeros and ones of computer code. 9500 museum visitors saw the show in 2008. It has received more comment card raves than any other program in the Museum repertoire. A typical comment: "Very entertaining AND educational!"





Talking Nano, a 6 DVD video set, has been receiving excellent reviews.

Sir Harry Kroto wrote in Materials Today, "...an excellent overview with something for almost everyone – a very good set of presenters who are not only leaders in the field but also good communicators."

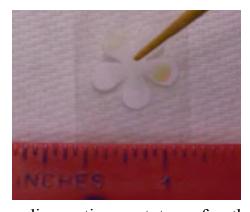
Andrew Maynard, Chief
Science Advisor of the
Wilson Center Project on
Emerging
Nanotechnologies wrote:
"An excellent
resource...You can't help
thinking.... "Wow - so
this is what nano is all
about!"

Info and copies at: www.talkingnano.net

Miniaturizing Assays: Adapting Paper Diagnostics for the K-12 Classroom



Graduate student Andres Martinez talks with teachers Tray Sleeper and Rebekah Ravgiala about the science and engineering behind paper diagnostics.

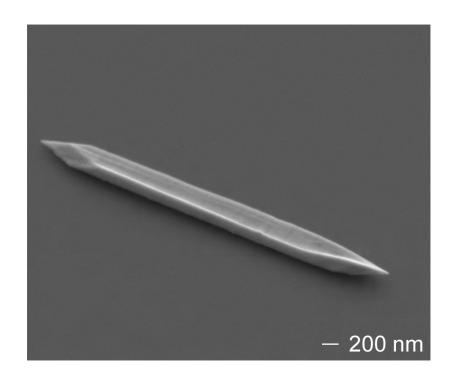


Paper diagnostics prototype for the K-12 classroom made with chromatography paper and a craft punch. Reagents for standard assays for pH and protein are dotted on each "petal" and sample is loaded in the center with a toothpick. Capillary action causes the sample to travel to all petals; a color change indicates pH and protein.

Research Experiences for Teachers participants worked with researchers in the George Whitesides laboratory to translate current research on paper diagnostics for the K-12 classroom. Current classroom assays for protein, pH, and carbohydrates are time- and resource-intensive; adapting these assays to paper platforms can save classroom and preparation time. Teachers have prepared lesson plans on the social implications of paper diagnostics, a scientific inquiry "who-done-it," and the reagent and cost savings of using paper diagnostics.

Single-Crystalline Gold Nanowires that Guide Light at the Nanoscale

Benjamin J. Wiley, Darren J. Lipomi, Jiming Bao, Federico Capasso, and George M. Whitesides

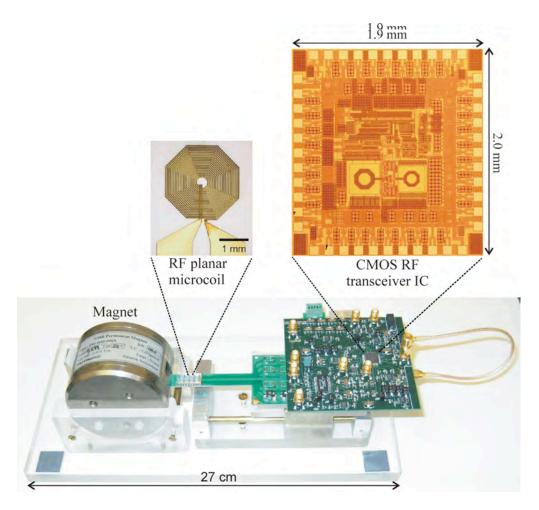


We developed a method to make nearly atomically smooth, single-crystalline gold nanowires by slicing 100-nm-thick crystals grown in solution into 100-nm-thick sections with an ultramicrotome. These wires can guide light at the nanoscale for longer distances that rougher, poly-crystalline nanowires. Nanowires with sharp tips act as nanoscale antennas that selectively guide light at their resonance frequency. This study may lead to the development of nanoscale optical interconnects that improve the speed of computer processors.

CMOS NMR RF Biomolecular Sensor

Donhee Ham

1ST Prototype Image



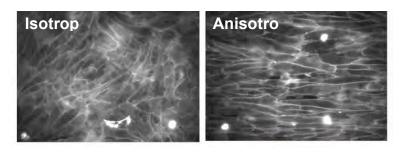
This system (2 kg) using a fist-size magnet is 60x lighter, 40x smaller, yet 60x more mass sensitive than the state-of-the-art commercial NMR system. The silicon RF chip contains most RF electronics, except for a power amplifier. The NMR coil was separately fabricated at Harvard.

Anisotropic Conduction in Engineered Myocardium

Kevin Kit Parker

regenerated We the structure of healthy and diseased cardiac tissue at the micro- and nanoscale by precisely controlling the orientation of individual myofibrils within the cardio-myocytes. This required maintaining coupling and organization multiple spatial across scales from nanometer scale actin and myosin micrometer motors to scale myofibrils up to the centimeter scale of functional cardiac muscle. The propagation of action pot-

2-Dimensional Engineered Cardiac Tissue (Membranes Stained w/ Voltage Sensitive Dye)



Action Potential (2 Hz Pacing) Conduction Map (Isochrones)

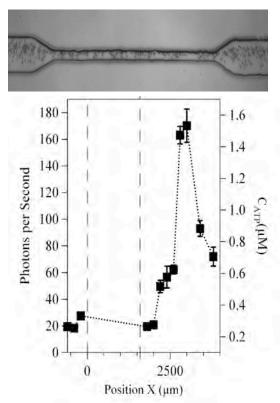
entials through the engineered cardiac tissue was observed with an optical mapping system to quantify the function of nanoscale ion channels in the cell membrane and the coupling of gap junctions that interconnect the cardiomyocytes together to form a continuous muscle tissue.

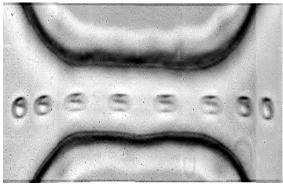
Crystal Ripplinger, Adam W. Feinberg and Kevin Kit Parker Disease Biophysics Group, Harvard University

Shear-induced ATP Release from Red Blood Cells

Howard A. Stone

Red blood cells are capable of significant deformation as they migrate through the microcirculation. When cells experience significant shear stress they release ATP, which is known to act as a signalling molecule. We studied this kind have mechanotransduction problem using a microfluidic constriction through which red blood cells flow (upper right). The release of ATP is measured down-stream of the constriction using a biolumreaction (light inescent released when ATP is present, middle figure). Fin-ally, in order to better understand the interplay of cell deformation and ATP release we performed similar experiments but visualized the using high-speed video





(**lower right**). In this way we were able to learn more about the possible steps in the release of ATP from sheared red blood cell.

First-Principles Simulation of **Electron Injection in Photovoltaic Devices**

Efthimios Kaxiras

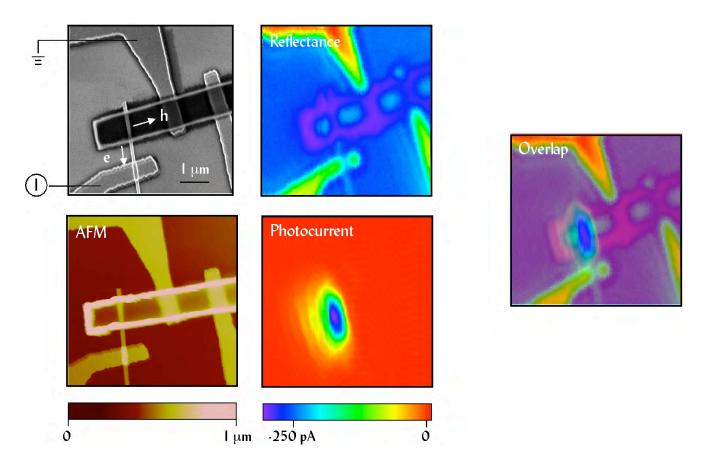
We have developed We have developed a computational method to treat the electron dynamics in excited states Time-dependent based on Density Functional Theory (TDDFT), coupled to ab initio molecular dynamics simulations. The 8.0 method is verv efficient and Injected Electrons (e) useful for a variety 0.6 problems of including electron 0.4 excitation. transport, atom collisand laser ion, 0.2 quantum control. In particular, it has been 50 100 applied address to Time (fs)

injection dynamics at the organic molecule/oxide electron semiconductor inter-face after photon adsorption in photovoltaic device. The figures show that electron can inject from the pigment to the semiconductor region within 100 fs, consistent with experimental measurement. Therefore a TiO₂ nanowire covered by dye molecules would work like a nanoscale tree with artificial leaves,

collecting sunlight and converting it into electricity.

SEM, AFM, Reflectance, and Photocurrent Images of a Single CdS-NW-P3HT Heterojunction

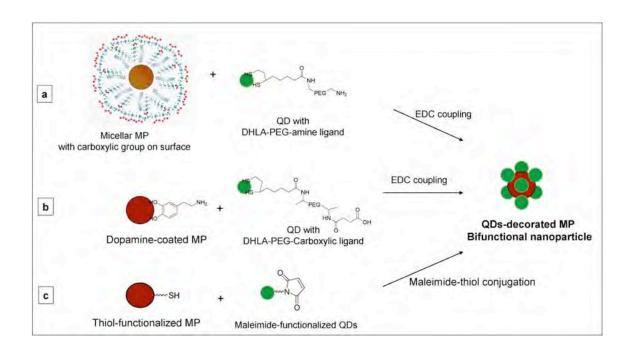
Hongkun Park



SEM (*upper left*), AFM (*lower left*), reflectance (*upper right*), and photocurrent (*lower right*) images of a single CdS-NW-P3HT heterojunction. These images clearly indicate that the photovotalic action of CdS-NW-P3HT solar cell occurs entirely at the junction between the CdS NW and the P3HT polymer strip. The analysis of the photocurrent data as a function of laser wavelength provides information on the charge separation efficiency as a function of photon energy.

Design and Synthesis of Fluorescent-Magnetic Nanoparticle Heterostructures

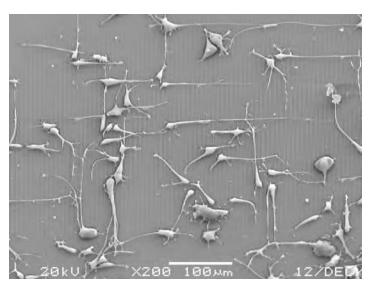
Moungi Bawendi Massachusetts Institute of Technology



We have designed and developed novel coatings on magnetic nanoparticles that allow them to be as small as possible but still retain the high magnetic properties that are desirable for applications ranging from biological imaging to magnetic force manipulation. We have also designed a methodology to combine these particles with fluorescent semiconductor nanoparticles (quantum dots) to create nanoparticle heterostructures that are both magnetic and fluorescent.

Controlling Cellular Morphology and Assembly Using Engineered Nanostructured Substrates

Joanna Aizenberg

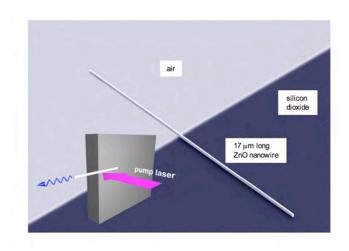


Nanopost arrays with tailored size, spatial distribution, and chemistry were fabricated to control stem cell differentiation. Such nanostructures seem to induce distinct morphocharacteristics logical in stem cells that resemble neuronal architectures. Further studies

are underway to utilize the nanopost arrays in a reciprocal system that illicits cellular responses via topographical, chemical, and mechanical actuation. This approach can be used as a platform to probe cell-matrix interactions by mapping cell-matrix forces, as well as to direct cell behavior, for example, to form complex cellular networks in neural chips, enhance phenotype purity in stem cell lineage specification or illicit tissue-specific cell behavior for other regenerative medicine and tissue engineering applications.

Semiconductor Nanowire Lasers

Federico Capasso



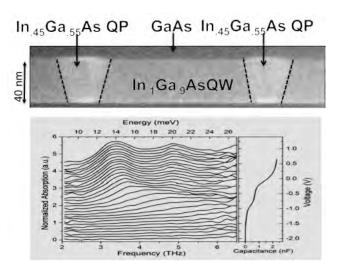
We have measured, for the first time, the output power of a single semiconductor Zinc Oxide nanowire laser emitting in the ultraviolet. The figure shows the experimental configuration: A nanowire, partially suspended in air, is excited uniformly along its entire

length and the emission is collected from one end, at 90° from the excitation beam, using a silicon detector. This measurement provides a useful benchmark for the development of semiconductor nanowires as components of future integrated photonic circuits. Furthermore, our unique geometry can be used for the detailed characterization of the near-field and far-field emission of nanowire lasers, which is instrumental for a full understanding of nanowire lasers as well as for their optimization.

A Tunable Quantum Post Terahertz Absorber

Pierre M. Petroff University of California, Santa Barbara

We have developed the first intrasubband absorber with 3-D confinement in the Terahertz (THz) range. The self-assembled quantum post (QP) is a short quantum wire terminated at each end by a quantum dot (see the cross section TEM micrograph). The QPs are loaded with electrons by integrating them into a MISFET structure. The peaks in the capacitance — voltage spectra (shown



in the figure) detect the onset of the electron loading in the QPs and quantum Absorption well. spectra taken from a sample with 30 high QPs nm (see the figure) demonstrate THzabsorption at voltages corresponding to the presence of electrons in the QPs. Moreover, the field tunable absorption associ-

ated with the quantum con-fined Stark effect is also observed. The width of the QPs absorption is associated with their lateral size and shape distribution.

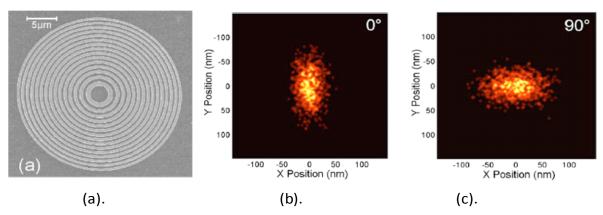
Our interest in these nanostructures stems from the possibility of confining electrons into a 3-D nanostructure. This feature could be very advantageous for developing room temperature emitters in the THz range. To this effect we are developing a quantum post quantum cascade laser.

This research was performed in collaboration with M. Sherwin, C. Pryor, Dominik Stehr, C. Morris, Hyochul Kim and Tuan Ahn.

Spring Constant Modulation of a Microfabricated Optical Tweezer

Ethan Schonbrun and Kenneth Crozier

Optical tweezers have become important tools in the biological sciences. Trapped particles can be used to exert forces on their local environments with calibration performed with Hooke's Law. Fresnel zone plates can produce highly elliptical focal spots. Using this feature, we have demonstrated a method for modulating the spring constant of an optical trap by rotating the polarization. A Fresnel zone plate was fabricated (Figure a). By measuring the positions of trapped particles we obtained two-dimensional histograms of particle position (Figures b, c) for different input polarizations. The results demonstrated that the spring constant along a given direction could be modulated.

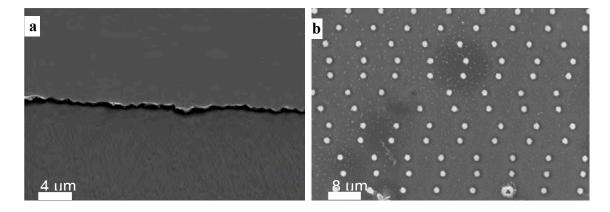


(a) Scanning electron micrograph of Fresnel Zone Plate optical tweezer, consisting of concentric gold rings (50-nm thick) on a microscope slide. (b), (c) Histograms showing positions of trapped particle at 1000 instants in time, for two different input polarizations.

Category: a). Discoveries at and across the frontier of science and engineering.

Fabricating Novel Nonlinear Optical Platforms

Eric Mazur



Nonlinear optics is an exploitable phenomenon for creating an all-optical-switch. When this technology is scalable, monolithic photonic chips could be produced enabling an all-optical-network. The Mazur group has begun to structure titanium dioxide (TiO₂) is an attractive platform because of its exceptionally high nonlinearity (55 times greater than silica) and its high index of refraction, which produces excellent light confinement. (a) Preliminary etchings of TiO₂ on silica. He has recently been applying the same techniques to fabricate metal structures. (b) Preliminary femtosecond laser-based nanostructured dots of silver on glass substrates.

Femtosecond-laser based nanofabrication is scalable and can be used to manufacture large volumes of nano- and microstructures quickly and inexpensively. The femtosecond laser-based techniques can also be used to make three-dimensional electrical circuits, optical devices, and biological structures.

Imaging and Atomistic Modeling of Defects on Surfaces: CI on Au(111)

Cynthia M. Friend

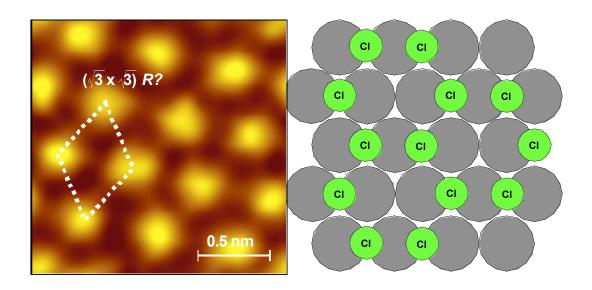
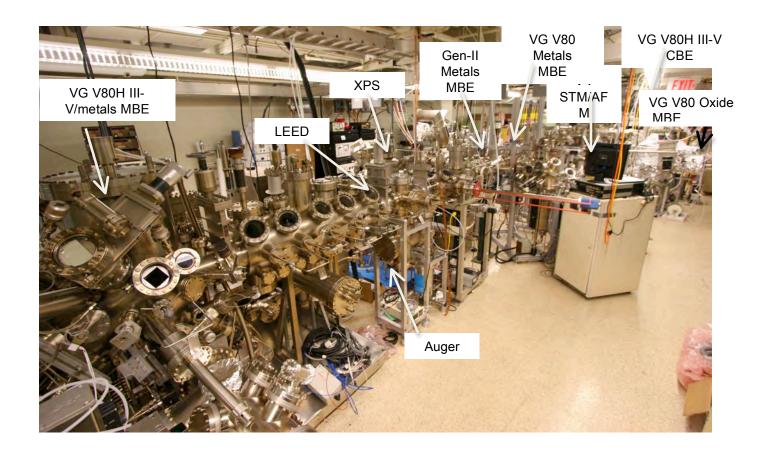


Image of chlorine on Au(111) (left) obtained using STM and the corresponding computed structure based on density functional theory. In this work, we show that Cl induces the release of Au from the surface at higher coverage, leading to corrosion and structural changes in gold used for, e.g., interconnects and in sensors. The work shown is a joint effort of the Friend and Kaxiras groups.

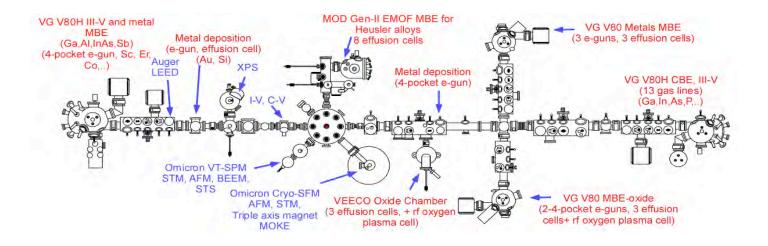
New in-situ Growth and Characterization System at UCSB

Arthur Gossard



New in-situ Growth and Characterization System at UCSB

Arthur Gossard



Extensive in-situ growth and atomic level characterization

Enhanced growth capabilities 5 interconnected MBE/CBE systems for III-Vs,

metals and oxides – allowing new nanocomposites including other RE-V and transition metal-V and t

ransition metal-III compounds

Determination of structure and chemistry at the atomic level at different stages of growth

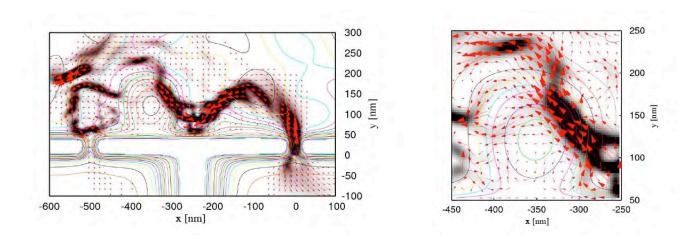
STM/AFM, Auger, XPS, LEED, RHEED

Atomic level electronic and magnetic properties – STM/STS, BEEM of nanocomposites

both plan view and cross-section (VTSTM 50-800K) and as a function of applied magnetic field (Cryo-SFM ~4-300K, MFM, Spin polarized STS, MOKE)

Wave Packet Approach to Semiconductor

Heller, Westervelt, Kramer, Parrott

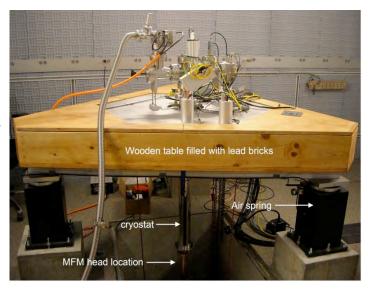


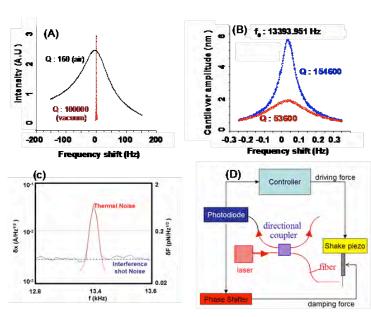
By launching wave packets the size of the thermal length, a thermally averaged transport calculation can be performed in one shot, including the presence of gate potentials, magnetic fields, random impurities, donor atom fluctuations, etc. This new theoretical tool has been successfully applied to a wide range of problems, including transconductance in a 2DEG and a new approach to the Integer Quantum Hall Effect.

High Resolution Force Microscope

Jennifer Hoffman

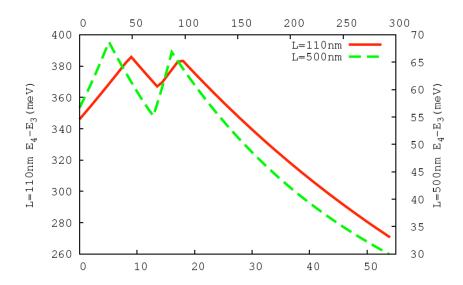
Magnetic imaging at the subnanometer scale is challenging. We are con-structing a new cryogenic force microscope employing a vertical cantilever and a novel AC magnetometry technique with planned magnetic force resolution of subpicoNewton and spatial resolution of sub-nanometers. Our force microscope will be applied to exploit the technological potential of superconductors, multi-ferroics, and magnetic nanoparticles. collage shows a photo of the fully assembled microscope system, measured noise spectra, and the result of an active Q control through capacitive coupling.





Imaging and Manipulating Electrons in a One-dimensional Quantum Dot with Coulomb Blockade Microscopy

J. Qian, B.I. Halperin, and E.J. Heller



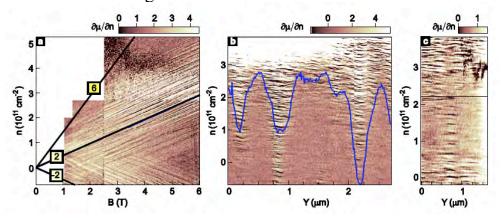
Motivated by experiments by the <u>Westervelt</u> group, which used a charged scanning tip to probe the electronic state of quantum dots formed on a segmented nanowire we have calculated shifts in Coulomb blockade peak positions for conduction through the nanowire, as a function of the tip position and potential. We show that if the tip is sufficiently close to the wire, one can distinguish a high-density electron liquid from a Wigner-crystal-like state by scanning with a weak tip potential. In the opposite limit, with a strongly negative tip, the potential depletes the electron density under the tip and divides the quantum dot into two segments. Moving the tip can push individual electrons from one segment to the other, which can be tracked by monitoring shifts in the conduction peaks.

Energy difference between ground states of N = 4 and N = 3 electrons, as a function of probe position x_0 , for wire lengths 110 nm and 500 nm. Tip charge is in the strong limit.

Measured Spectrum of Localized States in Graphene

Amir Yacoby

Particle localization is an essential ingredient in quantum Hall physics. In conventional high mobility two-dimensional electron systems Coulomb interactions were shown to compete with disorder and to play a central role in particle localization. Here we address the nature of localization in graphene where the carrier mobility, quantifying the disorder, is two to four orders of magnitude smaller. We image the electronic density of states and the localized state spectrum of a graphene flake in the quantum Hall regime with a scanning single electron transistor. Our microscopic approach provides direct insight into the nature of localization. Surprisingly, despite strong disorder, our findings indicate that localization in graphene is not dominated by single particle physics, but rather by a competition between the underlying disorder potential and the repulsive Coulomb interaction responsible for screening.

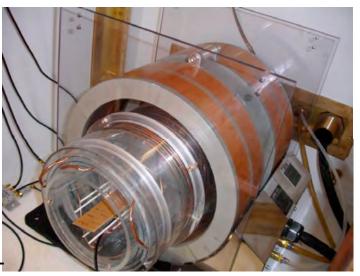


a. Color rendition of the inverse compressibility measured as a function of average carrier density (controlled using the back gate) and external magnetic field. The measurement is taken at a single location above the flake. Localized states in this measurement appear as dark lines that run parallel to the filling factor. **b.** Color rendition of the inverse compressibility measured along a line across the graphene flake and as a function of average carrier density. Localized states in this measurement appear as dark horizontal lines spanning a small spatial extent determined by the localization length or by the resolution limit of the tip. The solid line indicates the carrier density profile along the same line extracted from the surface potential measurements. **c.** Localized state spectrum of a single dot. The level spacing is inversely proportional to the size of the dot and yields a measured dot size of 60 nm.

Ultra-Low Field Magnetic Resonance Imaging of Hyperpolarized Nuclei

Charles Marcus

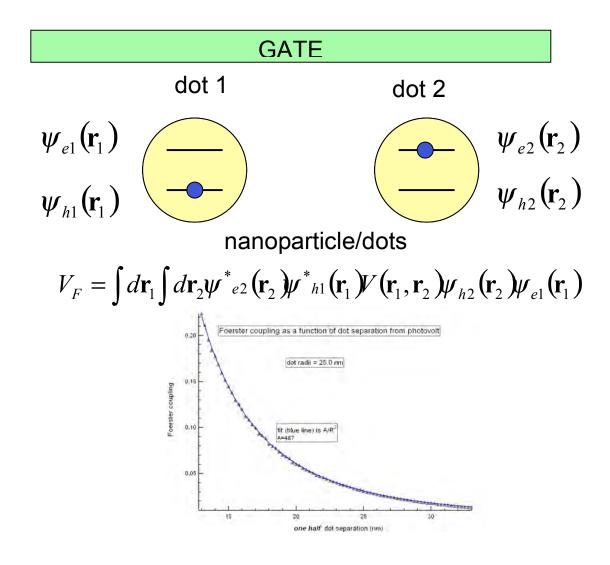
Room temperature hyperpolarization of using nuclei the effect Overhauser offers significant signal enhancement over the thermal nuclear spin population. We have designed and con-



structed a low field magnetic resonance imager capable of operating below at 50 mT. This system also accommodates an electron spin resonance coil operating at 300 MHz, allowing for *in vivo* hyperpolarization at frequencies transparent to living tissue. Using this system, we have shown an order of magnitude enhancement in the signal obtained from protons in water due to hyper-polarization.

Exciton Transfer via Förster

Michael Stopa



Similar to quantum dot, we can calculate electronic structure of confined excitons taking gate into account via boundary conditions on Poisson equation.

7. STRATEGIC RESEARCH PLAN

Our Center develops tools to study nanoscale systems. We would like to control electrons and photons inside nanostructures for new nanoelectronic and nanophotonic devices, and to investigate how biological systems function at the nanoscale using techniques from the Physical Sciences. Three Research Clusters address these goals:

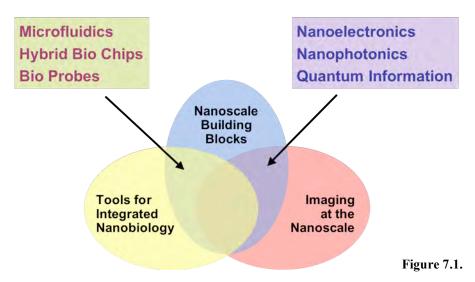
Cluster 1: Tools for Integrated Nanobiology builds bridges between the Physical Sciences, Biology and Medicine. Powerful new tools for manipulating and testing biological cells and tissues can be made using microfluidic systems, soft lithography, and semiconductor technology. Biology and Medicine offer an enormous range of engaging problems in functional biological systems, and the opportunity to think about "hybrid" systems that combine biological and non-biological components.

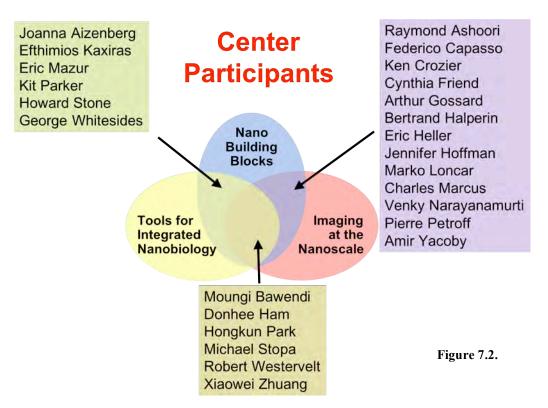
Cluster 2: Nanoscale Building Blocks makes new classes of nanostructures that exhibit size-dependent properties. We synthesize structures with unconventional shapes, as well as zero, one- and two-dimensional nanostructures including nanoparticles, nanowires, and heterostructures. New materials are introduced, including oxide semiconductors and metal chalcogenides. These nanoscale building blocks are promising for nanoelectronics and nanophotonics as well as for biosensors.

Cluster 3: Imaging at the Nanoscale explores new ways to image the quantum behavior of electrons and photons inside nanostructures using custom-made scanning probe microscopes, including cooled instruments. Imaging is an essential tool for the development of nanoelectronics, nanophotonics, and qubits for quantum information processing.

The desired outcomes for our Center's research are outlined in Figure 7.1. They are in two areas: Biology and medicine are addressed by the *Tools for Integrated Nanobiology* and *Nanoscale Building Blocks* research clusters. The outcomes are in the fields: *Microfluidic and Hybrid BioChips*, and *BioProbes*. Electronic and optical systems are

Research OutcomesOverlap of Research Areas





addressed by the *Nanoscale Building Blocks* and *Imaging at the Nanoscale* Clusters. The outcomes are in the fields of *Nanoelectronics*, *Nanophotonics*, and *Quantum Information Processing*. These applications will benefit society, and they are an important product of the Center's research program.

All of the Center's researchers currently work in more than one cluster, as shown by the Venn diagram in Fig. 7.2. This overlap has increased substantially since our Center was created in 2001, and it is good evidence of the benefits of collaborative research. The overlap between different research specialties creates exciting new topics, described in **Section 9 – Research Program**.

In the paragraphs below we show how the Center's participants work together to address potential outcomes of their research:

Microfluidic and Hybrid BioChips

Joanna Aizenberg (SEAS	Efthimios Kaxiras (Physics &	Robert Westervelt (SEAS &
	SEAS)	Physics)
Federico Capasso (SEAS)	Kit Parker (SEAS)	George Whitesides
		(Chemistry)
Donhee Ham (SEAS)	Howard Stone (SEAS)	Xiaowei Zhuang (Chemistry
		& Physics)

The investigators in this area create new microfluidic and hybrid electronic/microfluidic chips for applications in Biology and Medicine. George Whitesides is a pioneer in microfluidics and soft lithography. Microfluidic systems create biocompatible environments for the study of cells and can be used to create lab-on-a-chip systems for medical analysis. Whitesides works closely with fluid dynamicist Howard Stone, Joanna

<u>Aizenberg</u>, <u>Federico Capasso</u>, <u>Robert Westervelt</u> and other members of this group. <u>Joanna Aizenberg</u> is an expert in biomaterials and microfluidics. <u>Kit Parker</u> studies the behavior of cells in a microfluidic system using optical and scanning probe microscopy. <u>Xiaowei Zhuang</u> develops techniques for imaging viruses and proteins inside biological systems, and <u>Efthimios Kaxiras</u> simulates the behavior of biomolecules. Hybrid CMOS/microfluidic chips that combine biocompatible microfluidics with integrated circuits and optoelectronics have been created by <u>Donhee Ham</u> and <u>Robert Westervelt</u>, and <u>Federico Capasso</u> makes hybrid optical/microfluidic systems for sensing.

BioProbes

Joanna Aizenberg (SEAS)

Hongkun Park (Chemistry & George Whitesides (Chemistry)

Moungi Bawendi (Chemistry, MIT)

Efthimios Kaxiras (Physics & Michael Stopa (NNIN, SEAS)

Hongkun Park (Chemistry & George Whitesides (Chemistry)

Xiaowei Zhuang (Chemistry & Physics)

A group of Center investigators use probes based on nanoscale objects of different types to sense and image biological systems. <u>Joanna Aizenberg</u>, <u>Moungi Bawendi</u>, <u>Hongkun Park</u> and <u>Xiaowei Zhuang</u> develop nanoparticles and nanowires that can be biologically functionalized. <u>George Whitesides</u> is functionalizing interior surfaces of microfludic systems with biologically active materials. <u>Kit Parker</u> has developed an atomic force microscope tip that can selectively bind certain proteins and act as a scalpel for nanosurgury on biological cells. In related theoretical work, <u>Efthimios Kaxiras</u> and <u>Michael Stopa</u> simulate the motion of biomolecules.

Nanoelectronics

Raymond Ashoori (Physics, MIT)	Jennifer Hoffman (Physics)	Michael Stopa (NNIN)
Moungi Bawendi (Chemistry, MIT)	Marc Kastner (Physics, MIT)	Shriram Ramanathan (SEAS)
Cynthia Friend (Chemistry)	Charles Marcus (Physics)	Robert Westervelt (SEAS & Physics)
Arthur Gossard (Materials, UCSB)	Venkatesh Narayanamurti (SEAS & Physics)	Amir Yacoby (Physics)
Bertrand I. Halperin (Physics)	Hongkun Park (Chemistry & Physics)	
Eric Heller (Chemistry & Physics)	Pierre Petroff (Materials, UCSB)	

This group of investigators is developing new approaches in nanoelectronics. They combine the nanoscale building block synthesis and MBE growth with nanofabrication and theory to make, study, image and understand new types of nanoscale devices. Moungi Bawendi, Hongkun Park and our international collaborator Lars Samuelson are experts in the synthesis of nanocrystals and nanowires from new materials and their assembly into electronic devices; Cynthia Friend grows and studies two-dimensional materials with only one atomic layer on a surface. Shriram Ramanathan joined Harvard from Intel - he has developed new oxide semiconductors for nanoscale logic switches.

Arthur Gossard and Pierre Petroff use the MBE Lab at UC Santa Barbara to make new types of semiconductor heterostructures and self-assembled quantum dots. Using the nanofabrication facilities in Harvard's Center for Nanoscale Systems (CNS) and at MIT, Raymond Ashoori, Marc Kastner, Charles Marcus, Venkatesh Narayanamurti, Robert Westervelt and Amir Yacoby use e-beam and optical lithography to make a wide variety of nanoscale electronic devices. The nanoelectronic devices studied by this group range from transistors made from nanowires and self-assembled dots, to few-electron quantum dots, to open two-dimensional electron gas devices for studies in strong magnetic fields. Scanning-probe imaging techniques developed by Raymond Ashoori, Eric Heller, Jennifer Hoffman, Venkatesh Narayanamurti, Hongkun Park, Robert Westervelt and Amir Yacoby provide powerful tools to investigate how electrons move through these nanoscale devices. Collaborations with theorists Bertrand Halperin, Eric Heller and Michael Stopa allow the group to understand what the transport measurements and images mean.

Nanophotonics

Moungi Bawendi (Chemistry,	Marco Loncar (SEAS)	Xiaowei Zhuang (Chemistry
MIT)		& Physics)
Federico Capasso (SEAS)	Eric Mazur (SEAS & Physics)	
Kenneth Crozier (SEAS)	Pierre Petroff (Materials,	
	UCSB)	

The Nanophotonics group of investigators develops new approaches to photonics using nanoparticles, nanowires, nanofibers and imaging techniques. Moungi Bawendi is developing optoelectronic devices based on nanocrystal quantum dots. Using MBE growth, Pierre Petroff is making self-assembled InAs/GaInAs quantum dot and posts inside semiconductor heterostructures as photonic devices. Federico Capasso and Marco Loncar are developing photonic systems with embedded nanoparticles and nanowires. Eric Mazur is developing sub-wavelength diameter optical fiber devices. Federico Capasso and Kenneth Crozier have made plasmonic metal resonators in the form of optical antennas that spatially confine the electromagnetic field that are promising for subwavelength imaging using nearfield scanning optical microscope tips. Xiaowei Zhuang is developing subwavelength optical imaging techniques.

Quantum Information Processing

Bertrand I. Halperin (Physics)	Charles Marcus (Physics)	Robert Westervelt (SEAS & Physics)
Marc Kastner (Physics, MIT)	Michael Stopa (NNIN)	Amir Yacoby (Physics)

These investigators work closely with a group of international collaborators to implement and study systems for quantum information processing. Marc Kastner, Charles Marcus and Robert Westervelt have developed one-electron quantum dots to implement qubits, and are developing ways to manipulate individual spins. Theoretical understanding and simulations are provided by Bertrand I. Halperin and Michael Stopa. This group has strong international collaborations with Leo Kouwenhoven, Daniel Loss and Seigo Tarucha (see *International Collaborators* below).

Custom Scanning Probe Microscopes

Raymond Ashoori (Physics, Eric Heller (Chemistry & Robert Westervelt (SEAS & Physics) Physics)

Federico Capasso (SEAS)

Jennifer Hoffman (Physics)

Amir Yacoby (Physics)

Kenneth Crozier (SEAS)

Venkatesh Naryanamurti
(SEAS & Physics)

This group of investigators is well known for developing new imaging techniques to study of electrons and photons inside nanoscale systems, and for building their own scanning probe microscopes. These tools will be extremely useful for visualizing and understanding nanoscale devices and systems. Raymond Ashoori, Eric Heller, Robert Westervelt and Amir Yacoby use capacitive coupling between the tip of a cooled scanning probe microscope and the electrons to image their motion inside nanostructures. Jennifer Hoffman is constructing a cooled STM and a cooled high-spatial-resolution AFM to study high T_c superconductors and other materials. Venkatesh Narayanamurti has developed Ballistic Electron Emission Microscopy (BEEM) and Ballistic Electron Emission Luminescence (BEEL) Microscopy to study electron states inside nanostructures. Kenneth Crozier and Federico Capasso are developing a new type of Near-field Scanning Optical Microscope with a robust microlens tip that is equipped with a plasmonic metal resonator to more tightly focus the electromagnetic field.

International Collaborators

Yasuhiko Arakawa (Univ Daniel Loss (Univ Basel) Seigo Tarucha (Univ Tokyo, Tokyo, Japan) NTT, Japan)

Fabio Beltram (NEST, Italy) Lars Samuelson (Lund Univ,

Sweden)

Leo Kouwenhoven (TU Delft) Hiroyuki Sakaki (Toyota Tech

Inst, Japan)

Our Center has close collaborations with a strong group of investigators located overseas. Students and postdocs travel back and forth to carry out the research. <u>Hiroyuki Sakaki</u> is one of the founders of modern semiconductor physics through his development of superlattices and heterostructures. Yasuhiko Arakawa is a leader in photonics and heterostructure growth. <u>Leo Kouwenhoven</u>, <u>Daniel Loss</u> and <u>Seigo Tarucha</u> are very well known for their activity in quantum information processing. <u>Lars Samuelson</u> is a leader in nanowire synthesis and growth, and Fabio Beltram heads an impressive group at NEST.

Frontiers in Nanoscale Science and Technology Workshops

Our Center holds international *Frontiers in Nanoscale Science and Technology* (FNST) Workshops focused on nanoelectronics, nanophotonics, spintronics and quantum information processing. The workshops have attracted outstanding speakers, and they promote interesting and exciting discussions with the audience. Our Center provides scholarships to students and postdocs so that they can attend. The workshops they have proven to be a very effective way to connect students and postdocs with the newest ideas in nanoscience and technology.

Our fifth *Frontiers in Nanoscale Science and Technology Workshop* was held on January 6–8, 2008, at the Univ. of Basel in Switzerland, organized by <u>Daniel Loss</u> and <u>Robert Westervelt</u>. Bill Brinkman and Nobel prize winner Tony Leggett presented plenary talks.

Our sixth *Frontiers in Nanoscale Science and Technology Workshop* will be held at Harvard on May 29–31, 2009. Please see the poster below. An impressive group of speakers will participate, including leading investigators from academic and industry in Japan, Europe and the US.

We look forward to continuing this very effective series of workshops in the future.



8. RESEARCH PROGRAM, ACCOMPLISHMENTS, AND PLANS

Period: March 15, 2008 to March 14, 2009

RESEARCH PROGRAM

Overview:

Our Center develops tools to study nanoscale systems.

For electronics and photonics, we would like to synthesize new types of nanostructures, and visualize the motion of electrons and photons inside, using custom imaging techniques based on scanning probe microscopy.

For biology and medicine, we would like to understand how interacting cells behave as a system, and investigate the interior workings of cells, by developing powerful tools based on microfluidics and semiconductor technology.

Three Research Clusters address these goals:

Cluster I: Tools for Integrated Nanobiology builds bridges between the physical sciences, biology, and medicine. The physical sciences offer powerful new tools for manipulating and testing biological cells and tissues based on microfluidic systems, soft lithography, and semiconductor technology. In turn, biology and medicine offer an enormous range of engaging problems in functional biological systems, and the opportunity to think about "hybrid" systems that combine biological and non-biological components.

Cluster II: Nanoscale Building Blocks addresses the synthesis of new classes of nanostructures that exhibit size-dependent properties. An emphasis is placed on zero, one- and two-dimensional nanostructures, including nanoparticles, nanowires and heterostructures. Techniques to synthesize nanostructures from new materials are being developed, including oxide semiconductors and metal chalcogenides. These nanoscale building blocks provide new approaches for nanoelectronics and nanophotonics as well as sensors for biological systems.

Cluster III: Imaging at the Nanoscale explores new ways to image the quantum behavior of electrons and photons in nanostructures using custom-made scanning probe microscopes (SPMs). These instruments include cooled SPMs for the capacitive probing of electrons inside nanostructures, a cooled scanning tunneling microscope (STM), an STM equipped for Ballistic Electron Emission Microscopy (BEEM), and near-field scanning optical microscopes (NSOMs). These tools are used to develop and understand the behavior of nanoelectronic and nanophotonic devices.

CLUSTER 1: Tools for Integrated Nanobiology

Coordinator: George M. Whitesides

Donhee Ham (SEAS, Harvard) Howard A. Stone (SEAS, Harvard)

Efthimios Kaxiras (Physics & SEAS, Harvard)

Harvard)

Kevin (Kit) Parker (SEAS, Harvard)

Robert M. Westervelt (SEAS & Physics, Harvard)

George M. Whitesides (Chemistry, Harvard)

Xiaowei Zhuang (Chemistry, Physics, Harvard)

Collaborators: Rick Rogers (School of Public Health, Harvard) Giannoula Klement (Children's Hospital, Harvard), Ralph Weissleder (Medical School, Harvard), Mara G. Prentiss (Physics, Harvard), and X. Sunney Xie (Chemistry, Harvard)

Number of postdoctoral fellows: 4 Number of graduate students: 3 Number of undergraduate students: 3

Introduction

As biology begins to ask more quantitative and analytical questions about the nature of the cell, it needs new tools to study subcellular structures that have nanoscale dimensions. An important task is to build bridges between the physical and biological sciences. The physical sciences offer to biology new measurement tools and new procedures for analyzing the information obtained. In turn, biology offers to the physical sciences an enormous range of engaging problems, and stimulating examples of very sophisticated, functional biological systems. It also offers the opportunity to think about "hybrid" systems that combine biological and non-biological components.

The interface between the biological and physical sciences is one with enormous promise for fundamentally new science and, ultimately, technology. By supporting collaborations between investigators in the School of Engineering and Applied Sciences (SEAS), the Department of Chemistry and Chemical Biology, the Medical School, and the School of Public Health at Harvard, Cluster 1 will catalyze and expand a series of very effective collaborations across the physical-biological interface.

We expect three outcomes:

Tools for Cellular Biology and Tissue Culture: One of the major contributions that the physical sciences can offer to biology are new physical tools that can provide new kinds of information about cells and tissues.

The Science and Engineering of Interfaces between Animate and Inanimate Systems: This research will contribute to studies of cells in cell cultures, and to the assembly of groups of cells of the same or different types. In society, it will contribute to engineering the interface between patients and prostheses.

Tools for the Development of Drugs: The control over cells afforded by new microfluidic tools will be the basis for entirely new types of bioassay that will be important as the pharmaceutical industry moves away from information-poor animal assays in preclinical studies toward more informative studies based on primary human cells.

Miniaturized NMR System

Donhee Ham

Electrical Engineering, Harvard University

Collaborator: Ralph Weissleder (Mass. General Hospital)

Research Goal, Approach and Accomplishments. In this work [Cluster 1: Tools of Integrated Nanobiology], Donhee Ham's group, in collaboration with Ralph Weissleder's group at MGH, sought to develop a miniaturized NMR relaxometry system, by using a small, fist-sized magnet and an in-housed fabricated microcoil together with an RF transceiver integrated in a silicon chip. The ultimate goal was to build a portable NMR relaxometer, which can detect biomolecules for diagnostic purposes. We carried out this work successfully, and constructed the smallest complete NMR relaxometry system, which is 40 times smaller, 60 times lighter, yet 60 times more sensitive than a commonly-used, state-of-the-art commercial benchtop system [1]. Figure 8.1 shows the photo of our mini NMR system. Its functionality was demonstrated through proton NMR measurements in water, and via biomolecular detection.

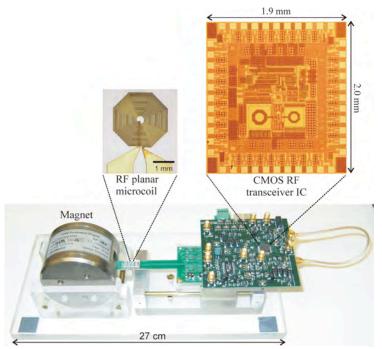


Figure 8.1. The CMOS mini NMR system [1].

The key challenge that we faced in this development was not just the integration of the RF transceiver, but to improve the performance of the integrated RF transceiver beyond what is typically required in larger NMR systems. This was because we had to overcome adverse conditions for **NMR** detection created by the lowquality magnetic field (weak strength of 0.5 Τ pronounced inhomogeneity) small, low-cost of the magnet, which was necessary for the system miniaturization.

The RF transceiver we designed includes front-end low noise amplifiers (LNA), variable gain amplifiers (VGA), mixers, and pulse sequencers in a heterodyning configuration with lock-in amplification element. The receiver part of the transceiver achieved an overall input referred noise of only 2.5 nV/Hz^(1/2), with which we were able to pick up NMR signals down to a few μV level. The transmitter portion of our transceiver was able to vary the power amplitude and pulse width in conjunction with a digital pulse sequencer, with which we were able to control the Rabi oscillation frequency with a proper pulse sequence to create the spin echo to overcome the

inhomogeneity of magnetic field for relaxometry. Figure 8.2 shows the RF transceiver architecture.

Figure 8.2 shows the detected spin echos where the NMR experiment was done with water protons. The top of Figure 8.2 is the spin echos when a smaller concentration of magnetic particles (0.1 mM) was put into the water. The bottom of the figure is the spin echos when a larger concentration of magnetic particles (1 mM) was put into the water. The magnetic particles spatially and temporally modulate spin precession frequencies, and hence accelerate spin-spin relaxation. The decreased spin-spin relaxation time T_2 with the increase of magnetic particle concentration is evident in Figure 8.2. Measured T_2 times with various particle concentrations match the theory.

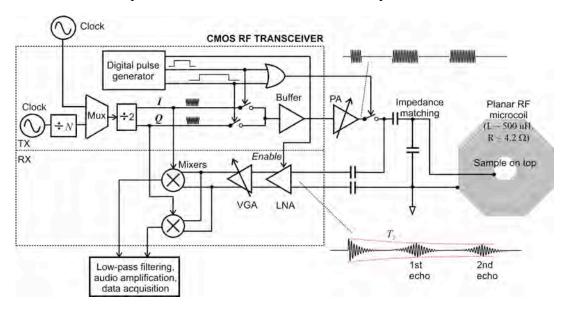


Figure 8.2. CMOS RF transceiver architecture used in the mini-NMR system.

Figure 8.3 shows the capability of our system as a biomolecular sensor. Magnetic nanoparticles coated with biotin that bind to avidin are put into a sample. If avidin exists in the sample (Fig. 8.3, *bottom*), the magnetic particles assemble into clusters [2]. These clusters reduce T₂, by accelerating the spin dephasing process. In the absence of avidin (Fig. 8.3, *top*), the magnetic particles remain mono-disperse in the sample, showing a smaller T₂ time in comparison to the case where avidin existed. The detection sensitivity for avidin is 20 fmol in mass, and 4 nM in concentration. The mass sensi-tivity is 60 times more than the commercial, state-of-the-art NMR relaxometry system. This detection sensitivity was limited by the assay, and our collaborator (Ralph Weissleder; MGH)'s newly developed assay can improve the detection level down to pM range. We also performed detection of folic acid, and are in currently the process of performing sensing experiments with various other biomolecules, including cancer marker proteins.

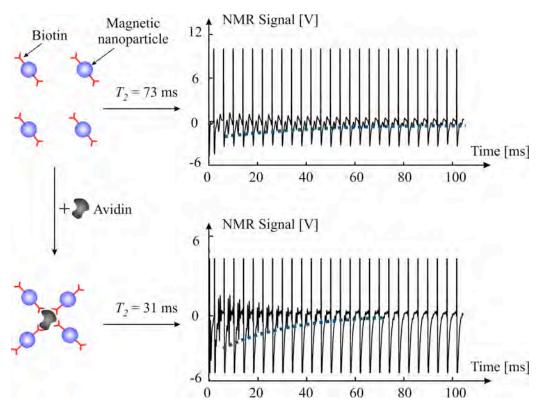


Figure 8.3. Experimental avidin detection using the CMOS mini-NMR system.

References

[1] Y. Liu, N. Sun, H. Lee, R. Weissleder, and D. Ham, *IEEE ISSCC*, 140–141 (2008).

[2] J. M. Perez et al., Nature Biotechnology 20, 816 (August 2002).

Multiscale Modeling of DNA Translocation through Nanopores

Efthimios Kaxiras

Physics and Applied Physics, Harvard University

Research Goal, Approach and Accomplishments

The goal of our research project is to develop an efficient computational method to treat the electron dynamics in excited states based on Time-dependent Density Functional Theory (TDDFT), coupled to *ab initio* molecular dynamic's simulations and apply it to address scientific problems in renewable energy research. The method could also be useful for a variety of problems including electron excitation, transport, atom collision, and laser quantum control. Using this method, which has been successfully implemented in a standard first-principle package SIESTA during 2008, we have demonstrated that the electron injection dynamics at the organic molecule/oxide semiconductor interface in hybrid photovoltaic device is very efficient: Electron can inject from the pigment to the semiconductor surfaces within 100 fs, consistent with recent experimental measurement. Therefore a TiO₂ nanowire fully attached with dye molecules could work like a tree at nanoscale for collecting sunlight and converting it into electricity.

More specifically, we plan to study the structural properties and electronic couplings between the semiconductor nanostructure (such as TiO₂ or ZnO nanowires) and the natural dye molecules *at the molecular level*. Deeper insights into charge injection mechanism will help us engineer the dye/nanostructure interface with guidance, towards a better performance and higher solar-to-electricity efficiency in DSCs.

Early DSCs involve transition metal coordinated compounds (e.g., ruthenium polypyridyl complexes) as sensitizers because of their strong visible absorption, long

excitation lifetime and efficient metal-toligand charge transfer. Although highly effective (with the current maximum efficiency of 11%), the costive synthesis and undesired environmental impact call for cheaper, simpler, and safer dyes as The natural pigments, alternatives. including chlorophyll, caro-tene, and cyanin, freely available in plant leaves, flowers, and fruits, fulfill requirement. Experimentally natural dye sensitized TiO2 solar cells has reached a high efficiency of 7.1% and high stability.

Recent efforts in developing DSC has also made use of one-dimensional (1-D) nanowire and nanotube structures of semiconductor. Comparing to the commonly used nanoparticles, the 1-D nanowires (generically including

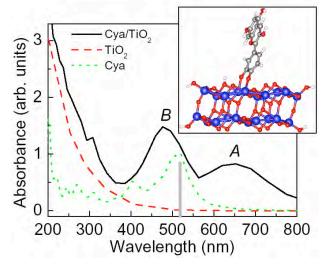


Figure 8.4. Optical absorption spectra of a TiO_2 nanowire (*inset*) with (solid line) and without (dashed line) sensitizing dye molecules. The calculated spectrum for a free cyanidin molecule is also shown (dotted line), together with the experimental peak position (vertical bar).

nanotubes) provide additional benefits in two aspects: 1) With its high length-to-diameter ratio and a total length reaching hundreds of micrometers comparable to visible light wavelength, its visible light scattering and absorption is much enhanced; 2) its 1-D geometry facilitates rapid, diffusion-free electron transport to the electrodes. Both effects have been verified in experiments. Nevertheless, the molecular mechanism and electronic coupling between a TiO₂ nanowire and a dye molecule, especially a natural dye, has never been addressed. Here we propose to study the coupling mechanism between the nanowire and natural dyes using quantum-mechanical methods and to provide a deep insight into charge injection mechanisms of natural-dye sensitized nanowire solar cells.

We are currently working on a model system, cyanin adsorbed TiO₂ nanowire. Our preliminary results show that visible light absorption is greatly enhanced upon dye adsorption, with maxima at 480 and 650 nm (Figure 8.4). Our study also reveals that the excited electrons can be injected into the TiO₂ conduction band ultrafastly in 72 fs, with negligible electron-hole recombination and energy dissipation, though the dye lowest-unoccupied-molecular-orbital (LUMO) locates 0.1–0.3 eV lower than the TiO₂ conduction band minimum, in contrast to the general belief. This extends our current understanding of the mechanisms of DSCs and may lead to new concept development in high efficiency solar cells. Further investigation on the effects of different nanowire orientation, facets, adsorption sites, surface defects and the performance of different dye molecules will be taken.

Methodology

We use density functional theory (DFT) and time-dependent DFT (TDDFT) to study the atomic and electronic structure at the dye/semiconductor interface. The ever-increasing computational capabilities and the development of improved algorithms have made them suitable to simulate relatively large systems (~200 atoms) with high accuracy. In particular, we are improving the efficiency of TDDFT simulations to study optical properties and electron injection at the dye/TiO₂ interface. We employ a local atomic basis-set representation and real-time propagation of single-particle wave functions. Time evolution of electronic states is coupled with the classical Newtonian motion of ions using molecular dynamics (MD).

This method has a multiscale feature. The timescale of the simulation ranges from attoseconds studying precise details of ultrafast processes, to hundreds of femoseconds. Electron evolution can be further coupled to traditional *ab initio* MD (without TDDFT), extending to picosecond simulation; and to classical MD with force fields obtained from *ab initio* calculations, which gives atomic dynamics on a scale of nanoseconds. This enhances greatly the ability of these approaches to address the real-world problems such as adsorption geometry and stability.

Practically, we have implemented the above method in SIESTA, a standard ground-state DFT package. We observed a **decrease in computing time by two orders of magnitude** and **four-fold reduction in memory requirements** when comparing with the popular real-space grid, real-time implementation of TDDFT (OCTUPUS) for calculations on excited small molecules. Its potential will be maximized with the development of parallel computing and order-N algorithms.

Molecular Robotics for Nanomanufacturing

Kevin (Kit) Parker

Bioengineering, Harvard University

Collaborator: Kenneth R. Chien (Massachusetts General Hospital)

International Collaborator: Andre Kleber (University of Bern, Switzerland)

Research Goal, Approach and Accomplishments

Our research has focused on two main goals over the past year: 1) To repeatably engineer and characterize two-dimensional cardiac tissue with precisely controlled micro-and nanoscale structure and 2) to engineer structurally organized neo-myocardium from a renewable cell source for cardiac regenerative therapies. Both of these projects have relied heavily on the tools and facilities available at Harvard's Center for Nanoscale Systems and are at the forefront of biology and engineering.

In the first project, we aimed to mimic the structure of healthy and diseased cardiac tissue at the micro- and nanoscale by precisely controlling the orientation of individual myofibrils within the cardiac myocytes. This requires maintaining coupling and organization across multiple spatial scales from nanometer scale actin and myosin motors to micrometer scale myofibrils up to the centimeter scale of functional cardiac tissue. Micron-scale designs were etched into silicon wafers using photolithographic techniques. These designs were then transferred to polydimethylsiloxane (PDMS) stamps, which were used to deposit extracellular matrix proteins onto cell culture substrates in the desired pattern. Neonatal rat ventricular myocytes were then seeded onto the substrates and the cells assumed the desired patterns. Three distinct tissue models were created (see Figure 8.5, A–C): Isotropic tissue (ISO) with disorganized myofibrils and myocytes similar to tissue observed in the infarct border zone following myocardial infarction,

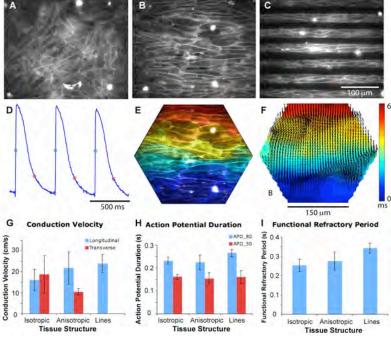


Figure 8.5. (A-C) Images of different micropatterned tissue structures stained with RH237. (**D**) Example optical action potentials with activation and repolarization times indicated. (E) Activation map of transverse propagation in an anisotropic monolayer overlaid on the tissue image. (F) Same activation map as (E) showing corresponding conduction velocity vector field. (G-I) Electrophysiological parameters as a function of tissue structure. Data are Mean ± StDev.

anisotropic tissue (ANISO) with uniaxially aligned myocytes similar to healthy myocardium, and one-dimensional lines of tissue (LINES) with enhanced uniaxial alignment but electrical discontinuity between the lines similar to increased fibrotic depositions in the heart found in several forms of heart failure. The electrophysiological properties of each tissue model were then evaluated using microscopic optical mapping with the voltage-sensitive dye RH237.

Several electrophysiological parameters were quantified including conduction velocity, action potential duration, and functional refractory period in each tissue type. Results indicate an increase in conduction velocity from 15 ± 4 cm/s in ISO tissue up to 22 ± 6 cm/s and 24 ± 4 cm/s in the ANISO and LINES, respectively. Complementary studies of contractility indicate that the LINES are also capable of generating more contractile force with less effective tissue area than the ISO or ANISO tissues. Thus, these studies are perhaps elucidating the functional role of microscale heterogeneities in adaptation of diseased hearts to continually meet the blood volume demands of the body. Additionally, these results demonstrate that microscale heterogeneities in the extracellular matrix can direct uniaxial cell alignment, allowing us to repeatably engineer myocardium with well-defined electrophysiological and contractile function.

The next project built upon the previous project by using many of the same techniques and innovations developed for engineering neonatal cardiac tissue to engineer neo-myocardium from a renewable, embryonic-derived stem cell source. Although there exists much interest in stem cell-derived therapies for cardiac regenerative medicine, thus far, organized cardiac tissue at the centimeter scale has yet to be produced from this cell source. We aimed to use micro-scale heterogeneities in the extracellular matrix to direct myofibrillogenesis uniaxially to create aligned, anisotropic tissue. As before, photo-lithographic techniques were used to deposit desired patterns of extracellular matrix proteins onto cell culture substrates and embryonic-derived murine cardiac progenitor cells were seeded onto the substrates to produce anisotropic neo-myocardium (Figure 8.6). Full characterization of electrophysiological and contractile properties of these tissues is ongoing. To our knowledge we will be the first group to demonstrate the creation of functional, spatially organized cardiac tissue from a stem cell source. This development is only made possible through the use of nanoscale engineering and fabrication techniques.

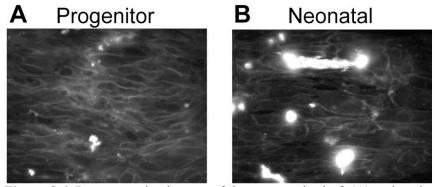


Figure 8.6. Representative images of tissue comprised of (**A**) embryoic-derived cardiac progenitor cells and (**B**) neonatal mouse ventricular myocytes (control) stained with RH237 dye, which highlights cell membranes.

Microfluidic Study of ATP Release of Red Blood Cells

Howard A. Stone

Materials and Fluid Mechanics, Harvard University

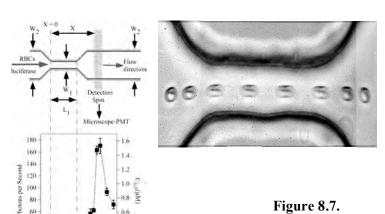
Collaborators: Anthony Aldykiewicz (Grace Construction Products); Andrew Belmonte (Penn State); Christopher Harrison, Claude Signer, Matthew Sullivan (Schlumberger); Alex Lips, K.P. Ananth (Unilever Research); Dionisios Margetis (University of Maryland); William Ristenpart (University of California, Davis); Chris Rogers (Tufts University)

International Collaborators: Manouk Abkarian (University of Montpellier, France); Armand Ajdari, Rene Gy, Julia Di Corleto (Saint-Gobain Research, Paris, France); Nicolas Bremond (ESPCI, Paris); Henrik Bruus (Technical University of Denmark); Lou Jing (Institute for High Performance Computing, Singapore); Eugenia Kumacheva (University of Toronto); Laurent Limat (University of Paris); Emmanuel Villermaux (University of Marseille, France); Metin Muradoglu (Koc University, Turkey)

Research Goal, Approach and Accomplishments

We have studied several distinct problems. Our main study has been shear-induced ATP release from red blood cells. This project lead to a new approach to using microfluidic to measure the kinetics of enzymatic reactions. In addition, we have studied one way in which electric fields can be used to separate vesicles with a focus on separating larger vesicles from a heterogeneous population of vesicles. Finally, we have studied over a two-year period the long time stability of submicron diameter gas bubbles that are also covered with an unusual regular polygonal nanopattern. These studies have spanned cellular-scale hydrodynamics, chemical kinetics, and multiphase materials relevant to nanofluidic and microfluidic systems.

Below I describe briefly two of these projects.



40 - 0.4 20 - 0.2

1. Red blood cells are known to release ATP when they experience shear stress. We have undertaken a systematic study of this problem using a microfluidic constriction to a) use a bioluminscent reaction to determine the time after onset of the shear stress when ATP is released (figure above, left) and b) use high speed

visualization to characterize the time dependent deformation of the cells in the same microfluidic constriction (figure above, right). With these experiments we then considered aspects of the mechanism for ATP release at the biophysical level of the deformation of the cell's membrane and the underlying spectrin network by utilizing recent advances in modeling. We believe we have made a novel and useful contribution to the mechanotransduction in this system.

2. We have completed a two-year study of the long time stability of submicron diameter gas bubbles that are covered with a surfactant system that essentially condenses on the interfaces. The gas bubbles are unusual as they are covered with a

regular polygonal nanopattern with typical length scale of 50 nm (see figure below). We also developed a thermodynamic model to

rationalize the observations.

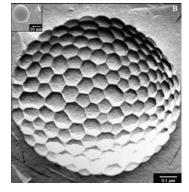


Figure 8.8

Simple Methods for Nanofabrication

George M. Whitesides

Chemistry, Harvard University

Collaborators: Arvi Samuel (Harvard University); Ilhan Aksay (Princeton University); Shawn Lockery (University of Oregon); Gabriel Lopez (University of New Mexico); Walter Fontana (Harvard Medical School); Younan Xia (University of Washington)

International Collaborator: Maria-Anita Rampi (University of Ferrara, Italy)

Research Goal, Approach, and Accomplishments

The research of our laboratory in the NSEC Center has evolved rapidly over the last funding period. It has focused on the continued development of the technique of nanoskiving—fabrication of nanostructures with an ultramicrotome—toward several different applications. This research has led to four peer-reviewed publications in 2008, which describe the fabrication of four new types of nanoscale building blocks and their applications: (i) Nanostructured organic heterojunctions for photovoltaics; (ii) conjugated polymer nanowires for chemical sensing; (iii) single-crystalline metallic nanowires for plasmonics; and (iv) electrically addressable, parallel metallic nanowires separated by a nanogap for electronics.

Nanostructured Organic Heterojunctions for Photovoltaics

This project concerned the fabrication of a nanostructured heterojunction of two conjugated polymers by a three-step process: i) spin-coating a multilayered film of the two polymers, ii) rolling the film into a cylinder (a "jelly roll") and iii) nanoskiving the film perpendicular to the axis of the roll. The conjugated polymers are BBL (e-acceptor) and MEH-PPV (e-donor). The procedure produces sections with an interdigitated junction of the two polymers. The spacing between the phases is determined by spin-coating (~15 nm to 100 nm) and the thickness of each section is determined by the ultramicrotome (100 to 1000 nm). The minimum width of the MEH-PPV layers accessible with this technique (~15 nm) is close to reported exciton diffusion lengths for the polymer. When placed in a junction between two electrodes with asymmetric work functions, and eutectic gallium-indium, EGaIn) the heterostructures exhibit a photovoltaic response under white light, although the efficiency of conversion of optical to electrical energy is low. (Lipomi, D.J., Chiechi, R.C., Reus, W.F., and Whitesides, G.M., Adv. Funct. Mater. 18, 3469–3477, 2008)

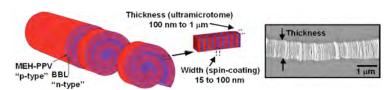


Figure 8.9. Schematic drawing of the jelly roll and SEM cross-sectional image of the actual structure.

Conjugated Polymer Nanowires for Chemical Sensing

The focus of this project was the fabrication of conjugated polymer nanowires by a three-stage process: i) spin-coating a composite film comprising alternating layers of a conjugated polymer and a sacrificial material; ii) embedding the film in an epoxy matrix, and nanoskiving; and iii) etching the sacrificial material to reveal nanowires of the conjugated polymer. A 100-layer film of two conjugated polymers was spin-coated from orthogonal solvents: MEH-PPV from chloroform, and BBL from methanesulfonic acid (MSA). After sectioning the multilayer film, dissolution of the BBL with MSA yielded uniaxially aligned MEH-PPV nanowires with rectangular cross sections, and etching MEH-PPV with an air plasma yielded BBL nanowires. The conductivity of MEH-PPV nanowires changed rapidly and reversibly by >10³ upon exposure to I₂ vapor. The result suggests that this technique could be used to fabricate high-surface-area structures of conducting organic nanowires for possible applications in sensing, and in other fields where a high surface area in a small volume is desirable. (Lipomi, D.J., Chiechi, R.C., Dickey, M.D., and Whitesides, G.M., *Nano Lett.* 8, 2100–2105, 2008)

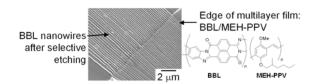


Figure 8.10. Image of conjugated polymer nanowires and chemical structures of materials used.

Single-Crystalline Metallic Nanowires for Plasmonics

This project demonstrates the sectioning of chemically synthesized, single-crystalline microplates of gold with an ultramicrotome (nanoskiving) to produce single-crystalline nanowires; these nanowires act as low-loss surface plasmon resonators. This method produces collinearly aligned nanostructures with small, regular changes in dimension with each consecutive cross section: A single microplate thus can produce a number of "quasi-copies"—delicately modulated variations—of a nanowire. The diamond knife cuts cleanly through microplates 35 µm in diameter and 100 nm thick without bending the resulting nanowire, and cuts through the sharp edges of a crystal without deformation to generate nanoscale tips. This paper compares the influence of sharp tips and blunt tips on the resonator modes in these nanowires. (Wiley, B.J., Lipomi, D.J., Bao, J., Capasso, F., and Whitesides, G.M., *Nano Lett.* 8, 3023–3028, 2008)

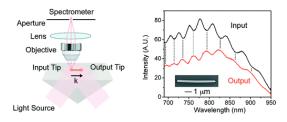


Figure 8.11. Schematic drawing of the experiment used to couple light into a single crystalline nanowire (left) and complementary spectra of the input and output ends of a nanowire (*right*).

Electrically Addressable, Parallel Metallic Nanowires

The goal of this project was the fabrication of arrays of parallel, electrically addressable metallic nanowires by depositing alternating layers of thin films of metal and polymer—both planar and topographically patterned—and nanoskiving the laminated structures. The structures that resulted from this process had two distinct regions: one in which parallel Au nanowires were separated by a minimum distance of 30 nm, and one in which the nanowires diverged such that the distal ends were individually addressable by low-resolution (≥10 µm) photolithography. Conductive polyaniline (PANI) was electrochemically deposited across the nanowire electrodes to demonstrate their electrical addressability, continuity, and physical separation. Before deposition, the wires were electrically isolated; with the PANI, they were electrically connected. After dry etching to remove the polymer, the gap between the nanowire electrodes returned to an insulating state. This procedure provides a method for making wires with dimensions and separations of <50 nm without the use of e-beam or focused ion beam "writing" and opens applications in organic and molecular electronics, chemical and biological sensing, and other fields where nanoscale distances between parallel conductive electrodes are desirable. (Dickey, M.D., Lipomi, D.J., Bracher, P.J., and Whitesides, G.M., Nano Lett. **8**. 4568–4573, 2008)

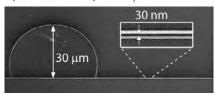


Figure 8.12. SEM image of two parallel nanowires separated by a nanogap of 30 nm, which diverge to an addressable separation of 30 µm.

CLUSTER 2: Nanoscale Building Blocks

Period: March 16, 2008 to March 14, 2009

Coordinators: Moungi Bawendi and Hongkun Park

Joanna Aizenberg (SEAS, Harvard)

Moungi Bawendi (Chemistry, MIT)

Federico Capasso (SEAS, Harvard)

Kenneth Crozier (SEAS, Harvard)

Cynthia M. Friend (Chemistry & SEAS, Harvard)

Arthur C. Gossard (Materials, UCSB)

Eric Mazur (SEAS, Physics, Harvard)

Hongkun Park (Chemistry, Harvard)

Pierre Petroff (Materials, UCSB)

Shriram Ramanathan (SEAS, Harvard)

International Collaborator(s): Lars Samuelson (Lund University, Sweden)

Seed Funding: Marco Lonçar (SEAS, Harvard)

Number of postdoctoral fellows: 3 Number of graduate students: 5 Number of undergraduate students: 3

Introduction

Tremendous progress has been made in the synthesis of nanoscale structures—nanocrystals, nanowires and nanotubes—that serve as building blocks for new devices and applications. However many challenges remain. They include the synthesis of nanostructures with well-defined sizes and shapes, the synthesis of new classes of materials, the in-depth characterization of newly developed nanostructures, the rational organization of these nanostructures into complex functional structures, and the fusion of nanoscale building blocks with state-of-the-art processing techniques, including e-beam lithography and focused-ion-beam sculpting, to build novel devices.

The *Nanoscale Building Blocks* cluster conducts a broad multidisciplinary, multiinvestigator research program that is designed to address these challenges. The proposed
research is built upon the participants' expertise in the synthesis and characterization
(both experimental and theoretical) of nanostructured materials. At the core of the
program is the *rational synthesis of new classes of nanostructures that exhibit new size- dependent properties* that are distinct from bulk materials, with an emphasis on
heterostructures and nanostructures with unconventional shape, as well as on zero-, oneand two-dimensional nanostructures made from new materials, including metal
chalcogenides. The *incorporation of nanostructures into novel device geometries*constitutes another important part. These new devices will be tested to characterize the
physical and chemical properties of the building blocks and to evaluate their
technological applicability. *Understanding the behavior of these nanoscale building blocks* through theoretical investigations is an important part of the effort, because it is
essential to advance the scientific and technological frontiers.

Localized Materials Deposition on a Superhydrophobic Nanowire Array

Joanna Aizenberg

Chemical Engineering, Harvard University

Collaborators: David Nelson, George M. Whitesides (Harvard University); Carol Lynn Alpert (Museum of Science, Boston); Tom Krupenkin (University of Wisconsin, Madison)

Controlling Cellular Morphology and Assembly Using Engineered Nanostructured Substrates

Research Goal, Approach and Accomplishments

Attaining appropriate cell morphology is essential for cell therapy since cell form modulates the interpretation of extracellular cues, impacting both phenotype stability and lineage specification. The goal of this project is to investigate stem cell growth and patterning on customized nanotopographies. We produced orthogonal arrays of high aspect ratio nanoposts with a range of nano- and micro-topographical features in Si and also replicated these structures in epoxide polymer using a PDMS molding technique. These structures were functionalized by fluorination, oxygen plasma, and/or passive protein absorption. Then murine mesenchymal stem cells were cultured on the substrates for up to 2 weeks and cell morphology was evaluated by SEM and live cell optical microscopy during seeding. By tuning the nanofeatures we have demonstrated reproducible control of cell gross morphological characteristics. We identified several distinct morphological differences for cells cultured on nanoposts with variable pitch. This included significantly more polarization and cellular projections on nanoposts relative to cells on unetched silicon. The highest percentage of polarized cell bodies and the longest projections were obtained on high aspect ratio nanopost arrays with diameter, height and spacing of 200 nm, 8 µm, and 2 µm, respectively. This post diameter and spacing was then investigated further using 40:1 aspect ratio "nailheads" and these samples illicited consistent alignment of cellular projections with the nanopost grid that was further enhanced by surface hydrophobicity.

The results indicate that nanopost arrays with tailored size, spatial distribution, and chemistry can be used to produce distinct morphological characteristics in stem cells that resemble neuronal architectures. Further studies are underway to utilize the nanopost arrays in a reciprocal system that both illicit cellular responses via topographical, chemical, and mechanical actuation, and at the same time probe the cell-surface interactions by mapping cell-matrix forces. Production of ordered bioactive surfaces by nanolithographic methods enables ordered bioactive surfaces with tunable nanoscale topology, chemistry and mechanical properties and is compatible with semiconductor fabrication. This approach can be used as a platform to probe cell-matrix interactions as well as direct cell behavior, for example, to form complex cellular networks in neural chips, enhance phenotype purity in stem cell lineage specification or illicit tissue-specific cell behavior for other regenerative medicine and tissue engineering applications.



Figure 8.13. SEM image of polarized and oriented stem cell growth on an orthogonal "nailhead" nanopost array. Cell extends and aligns with the underlying nanopost grid showing clear directional growth.

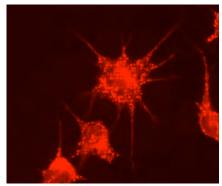


Figure 8.14. Murine stem cells on deformable epoxy nanopost arrays exhibiting post deformation and oriented cellular extensions at 0 and 45 degree orientations relative to underlying nanoposts.

Magnetic and Semiconducting Nanoparticle Systems: Properties and Devices

Moungi G. Bawendi

Chemistry, Massachusetts Institute of Technology

Collaborator: Rakesh Jain (Massachusetts General Hospital

International Collaborator: Luis Rivera (Univ. of Puerto Rico Mayaguez Campus)

Compact and Functional Magnetic-fluorescent Nanoparticles for Biological Applications

We have developed magnetic nanoparticles (MPs) with small hydrodynamic radii and containing various functional groups that are compatible for conjugation to biomolecules. Our aim is at making MPs that have a ligand shell that is as small as possible and expect to see an enhancement in many properties including an increase of their diffusion rate and a decrease of their steric hindrance to bio-molecule conjugation when compared to larger MPs.

The first type of MPs that we synthesized are amino-functionalized PEGylated MPs. These MPs where prepared from a coupling reaction of diamino-PEG with polyacrylic-coated micellar MPs as shown in Figure 8.15a. A TEM image of these MPs is shown in Figure 8.15c, showing that the core size remains the same as before the phase transfer process (Figure 8.15b). The size distribution of these MPs is shown in Figure 8.15d with an average radius of 10 nm. The R2 relaxivity of these particles was measured as 260 s⁻¹ (mM Fe)⁻¹.

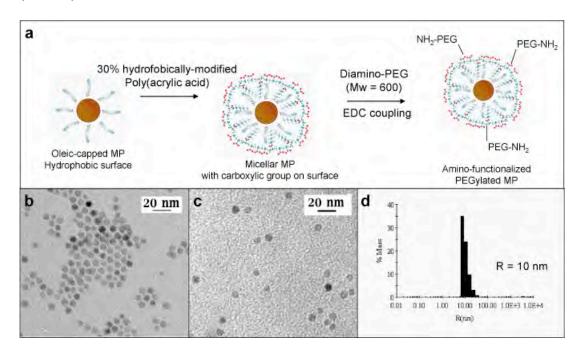


Figure 8.15. Preparation of amino-functionalized PEGylated MPs. (a) Schematic diagram for preparation of the MPs. (b) TEM images of as-synthesized hydrophobic MPs. (c) TEM images of amino-functionalized PEGylated MPs, and (d) size distribution of amino-functionalized PEGylated MPs from DLS.

The second types of MPs that we prepared are MPs coated with hydrocaffeic acid (HCA, Figure 8.16a). We aimed at making smaller MPs by using direct bonding between the ligands and surface of the MPs. HCA-coated MPs were prepared as shown in Figure 8.16a. The TEM images of the particles before (8.16b) and after (8.16c) ligand exchange show that the core MPs remain the same size. This type of MPs showed an average radius of 8.6 nm from DLS measurement. The size distribution of these MPs is shown in Figure 8.16d. These types of MPs have numerous carboxylic groups for conjugation.

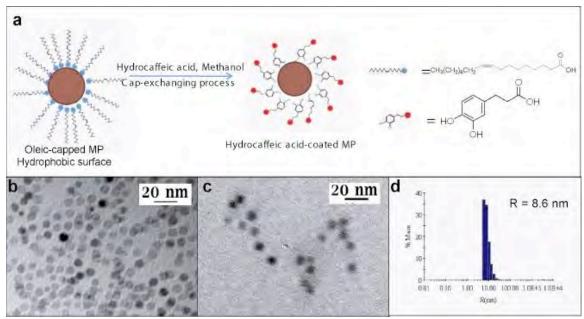


Figure 8.16. Preparation of HCA-coated MPs. (a) Schematic diagram for the preparation of the MPs. (b) TEM images of as-synthesized hydrophobic MPs, (c) TEM images of HCA-coated MPs, and (d) size distribution of HCA-coated MPs from DLS.

Thanks to the availability of many crosslinkers and heterobifunctional PEG derivatives, we can explore more reactive functional groups. Maleimide is one example that is interesting due to its specific reaction with thiol groups. We synthesized maleimide-functionalized MPs using Sulfo-KMUS (*N*-[κ-maleimidoundecanoyloxy]sulfosuccinimide ester) and maleimide-PEG-Amine as shown in Figures 8.17a and 8.17b, respectively.

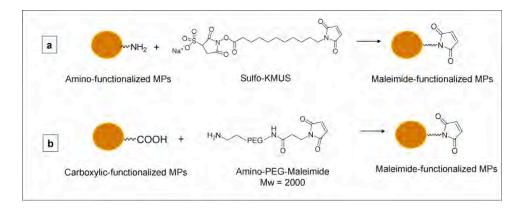


Figure 8.17. Preparation of maleimide-functionalized MPs. (a) prepared from aminofunctionalized PEGylated MPs and (b) from polyacrylic acid- and hydrocaffeic acid-coated MPs

We have conjugated these particles to some proteins and peptides, specifically Calmodulin and peptide RS20. Although the conjugation succeeded, a reduction of the excess of carboxylic groups is currently pursued.

We designed new biocompatible lidands with PEG polymer including carboxylic acid, hydroxamic acid, 1,2-diol, 1,3-diol and 1,2-enediol. We performed ligand exchange using newly designed 1,2-enediol that was inspired by a bio-organism, in order to overcome problems that the surfaces of the iron oxide nanocrystals were etched and precipitated out solution. When we characterized these surface engineered colloidal nanocrystals using DLS and TEM, the resulting nanocrystals show good chemical stability as well as good magnetic properties.

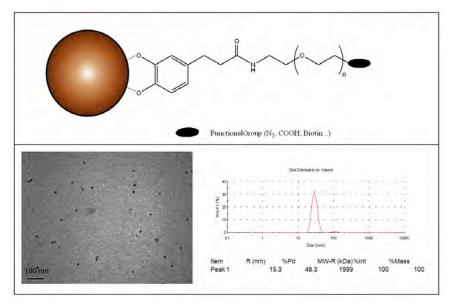


Figure 8.18. Schematic diagram of iron oxide nanoparticles with PEG functional group (*top*), TEM image in PBS (*bottom left*) and DLS result (*bottom right*).

With these MP building blocks, we are also currently making a new type of bifunctional nanoparticles by conjugating MPs with semiconductor quantum dots (QDs). We would like to made nanoparticles with superparamagnetic and photostable fluorescent properties. We have tried some conjugations, such as EDC coupling between polyacrylic-coated MPs and DHLA-PEG-amine QDs (Figure 8.19a) and between dopamine-coated MPs and DHLA-PEG-COOH QDs (Figure 8.19b.) The conjugations still need to be perfected. We are also exploring some reactions with other reactive groups, such as the reaction between thiol and maleimide as in Figure 8.19c.

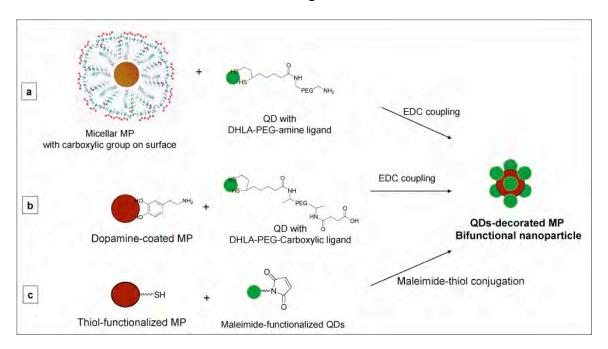


Figure 8.19. Schematic diagram for the preparation of QD-decorated MP bifunctional nanoparticles using (**a,b**) EDC coupling between carboxylic- and amino-functionalized nanoparticles and (**c**) conjugation of maleimide and thiol functional groups.

Semiconductor Nanowire Lasers

Federico Capasso

Applied Physics and Electrical Engineering, Harvard University

Collaborators: Kenneth B. Crozier, George M. Whitesides (Harvard University); Harry Atwater (Cal Tech); Franz Kaertner (MIT)

International Collaborators: Jerome Faist (ETH Zürich, Switzerland); Lars Samuelson (Lund University, Sweden)

Research Goal, Approach and Accomplishments

During the last year, <u>Capasso</u> and his group have continued a nanowire photonics program with the goal of developing efficient, room-temperature, electrically-pumped nanowire light emitters, which could form the basis for future integrated photonic circuits. After having developed several techniques for the fabrication of efficient nanoscale light-emitting diodes, and a deep understanding of their operation, they have turned to the understanding of more sophisticated light sources: nanowire lasers. Using optical excitation, they have observed for the first time the transition from amplified spontaneous emission to laser action in zinc oxide (ZnO) nanowires and have also elucidated the key dependence of the laser threshold on the nanowire dimensions, in particular the nanowire diameter. More importantly, they were able to use a "head-on" detection geometry to provide the first measurement of the output power of a single nanowire laser. Such a unique measurement geometry could also be used for the characterization of the near-field and far-field emission of nanowire laser, which is absolutely key for a full understanding as well as for the optimization of these devices.

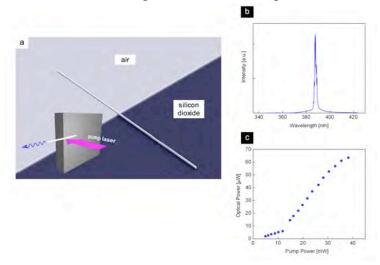


Figure 8.20. Semiconductor nanowire lasers: head on detection. (a) Scanning Electron Microscope (SEM) image of a 17 μm long, 244 nm in diameter, ZnO nanowire partially suspended in air and partially resting on a substrate (500 nm of thermally grown silicon dioxide). The nanowire is excited uniformly along its entire length, and the emission is collected from one end, at an angle of 90° from the excitation beam, using a silicon detector (see the schematic in the inset). (b) Output spectrum of the nanowire shown in (a) when pumped above the laser threshold with the frequency tripled output of a Nd:YAG laser (355 nm, with 6 ns pulses and a repetition of 500 Hz). (c) Peak optical power, uncorrected for the collection efficiency (10%), measured head on at the end of the nanowire shown in (a).

Microfabricated Water Immersion Zone Plate Optical Tweezer

Kenneth B. Crozier

Electrical Engineering, Harvard University

Collaborators: Jonathan Bernstein (Draper Laboratory); James Hogle (Harvard Medical School); Kimerling (MIT); Munb Wober (Zena Technologies); Joyce Wong (Schlumberger-Doll Research)

Spring Constant Modulation of a Microfabricated Optical Tweezer

Summary: At large NAs a micro-Fresnel zone plate produces a focal spot that is more elliptical than that produced by an objective lens with the same NA. Using this anisotropy we demonstrated a method for modulating the spring constant of an optical trap by rotating the linear input polarization.

Research Goal: The focusing element is often regarded as the most important component of an optical trap. Tightly trapped particles are strongly influenced by intensity gradients in the focal volume, making trapping performance sensitively dependent on the precise form of the intensity distribution. Previously, high performance optical traps have used microscope objective lenses. Fresnel zone plates, however, can focus light to smaller spots than microscope objectives with the same NA. The resultant larger intensity gradients make them of considerable interest for optical trapping.

Approach: In the past year, we have demonstrated that the anisotropy of a Fresnel zone plate optical trap can be used for spring constant modulation. We began by modeling the optical trap. Our Fresnel zone plate consisted of 15 concentric gold rings, each 50 nm thick, with the outermost ring having a diameter of 27 mm. For a laser wavelength of 976 nm, electron beam lithography can produce a zone plate with an NA that is extremely close to its maximum value, the refractive index of water n_{water} . With a focal length of $4\lambda_0/n_{water}$, the zone plate has an effective NA of 0.978 $n_{water} = 1.30$, which means that the maximum focusing cone angle is 78°. By comparison, the cone angle of a water immersion 1.2 NA objective and an oil immersion 1.4 NA objective is 64° and 68°, respectively. Figure 8.23(a) shows the zone plate and the maximum focusing angle. We found that at large NAs, the FWHM of the focal spot continues to decrease in the cross section perpendicular to the incident polarization toward its limit of approximately $0.36\lambda_0$ $/n_{water}$, as shown in the calculation of Figure 8.23(b) (lower curve). Surprisingly, in the cross section parallel to the incident polarization, we found that the width begins to increase at NAs above 0.9, shown in Figure 8.23(b) (upper curve). Note that in Figure 8.23(b), the NA is normalized to the refractive index of the immersion medium. Using the Debye integral method with the appropriate apodization factor, we analyzed the focal spot distributions of the zone plate and an aplanatic lens. With a fill factor of 1.73, the FWHM of the zone plate focal spot was found to be $0.426\lambda_0/n_{water}$ by $0.738\lambda_0/n_{water}$ in perpendicular and parallel cross sections, respectively. By contrast, for a 1.2 NA water immersion lens with the same fill factor, the FWHM is $0.537\lambda_0/n_{water}$ by $0.719\lambda_0/n_{water}$.

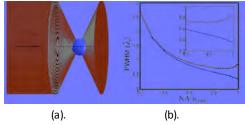


Figure 8.21. (a) Illustration of zone plate illumination and maximum focusing angle. (b) Full width at half maximum (FWHM) of a zone plate in perpendicular (lower curve) and parallel (upper curve) cross sections through the focus. At small NAs, the focus is circular, and then becomes increasingly elliptical at larger NAs. *Inset*. Expanded plot for NA ranging from 0.8 to 1.0.

Results and Accomplishments: We next fabricated and characterized Fresnel zone plate optical tweezers, with the goal of demonstrating the high degree of trapping anisotropy that our theoretical modeling had predicted. The zone plate optical tweezer, shown as Figure 8.22(a), was characterized by tracking the position of a trapped 1.1 µm diameter latex fluorescent sphere. A centroid algorithm was applied to the fluorescence image obtained from a CCD camera. By measuring the position of a single dried bead on a microscope slide, we found that the standard deviation of our position measurement was 2.5 nm. By measuring the positions of trapped beads over time, we were able to build up histograms of trapped particle positions. Figures 8.22(b)–(e) show trapped particle distribution for four different linear polarizations of the incident beam, where θ is defined as the angle between the incident polarization and the y axis. Images are taken at 30 Hz, with 1/64 s exposure times, for a total of 1000 frames. The centroid position of the bead for each frame is convolved with a Gaussian representing the measurement uncertainty of 2.5 nm and plotted. The results indicated that the trap spring constant was 2.75 times larger perpendicular to the incident polarization than along it. As shown in Figures 8.22(b)–(e), the elliptical focal spot distribution could be rotated by rotating the incident polarization. This confirms the goal of this study, showing that the spring constant along a given direction could be modulated.

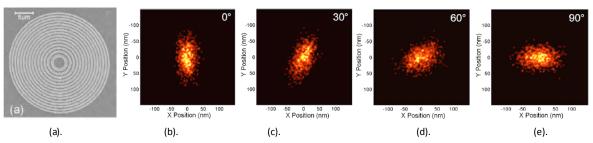


Figure 8.22. (a) Scanning electron micrograph of the gold on glass zone plate. (b)–(e). Histograms showing positions of trapped particle at 1000 instants in time. Particle positions are plotted over a 33 s duration at 30 Hz to map out the trapping potential of the elliptical. The orientation of the incident linear polarization is changed by rotating a half-wave plate.

Electronic Properties of 1-atom Layer MX_n Structures

Cynthia M. Friend

Chemistry and Applied Physics, Harvard University

International Collaborators: Katharina Al-Shammery (Oldenburg University, Germany), Marcus Bäumer (Bremen University, Germany)

Research Goal, Approach and Accomplishments

The objective of work in the <u>Friend</u> group is to synthesize and study new nanomaterials that have novel optical and chemical properties. Our current focus is to synthesize integrated nanostructures of semiconducting metal oxides, e.g., TiO₂, on Au substrates with the objective of increasing the efficiency of catalytic oxidation reactions using photons. We will use photons to mobilize O in our nanomaterials to create highly active oxidants. We also plan to develop synthetic methods for doping the oxide nanostructures in an effort to tune their band gap. This work builds on previous studies of controlled growth and imaging of TiO₂ nanostructures on Au funded in the NSEC (Figure 8.23). We are able to control the composition and structure by adjusting conditions for synthesis, which in turn tunes the electronic and optical properties of these materials. Our ability to control synthesis and reactivity depends on a understanding of how the structure of surfaces and of nanostructures evolves under reactive conditions, meaning in the presence of ambient gas and at elevated temperature.

During the past year, we have focused on understanding how to control morphology and atomic-scale structure of atoms on Au by using a combination of imaging and computation through a collaboration between the <u>Friend</u> and <u>Kaxiras</u> groups. As illustrated by the highlight below, we are able to study the release of atoms from surfaces and nanostructures when reactive species are present and as a function of temperature. This work is part of a larger effort to understand how the function and feature size of nanostructures may be limited by mobilization of atoms, which lead to corrosion. Besides

the case of Cl, illustrated in the highlight, we also show that S-containing species, e.g., thiols used in SAMs, and oxygen mobilize Au atoms.

The next phase of our work will combine our materials synthesis with our understanding of mobilization of atoms on surfaces. The goals of our future work are: (1) To mobilize reactive O atoms in metal oxide nanostructures to promote energy-efficient oxidation reactions; and, (2) to develop synthetic methods for doping metal oxide nanostructures so as to tune their band structure.



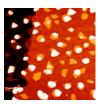


Figure 8.23. TiO₂ nanocrystals on Au(111) imaged using STM at two different magnifications. The images shown are 40 nm x 40 nm (*left*) and $100 \text{nm} \times 100 \text{ nm}$ (*right*).

Our future work will combine imaging and computation to obtain an atomic-level understanding of these processes.

Semiconductor Heterostructures for Nanoscale Devices

Arthur C. Gossard

Materials, University of California at Santa Barbara *Collaborators:* Lon Bell (BSST Industries LLC, Irwindale, California); Daniel Yap (HRL Laboratories, Malibu, California)

Research Goal, Approach and Accomplishments

Our research goal in this period was to produce and develop low-dimensional quantum structures and nanostructures by molecular beam epitaxy. We grew and performed structural and electrical characterization of planar, two-dimensional quantum materials for use and further study by other NSEC members. We also attempted to gain understanding of the so-called "switching" behavior that produces instabilities in the electrical characteristics of quantum structures on certain AlGaAs/GaAs wafers. We grew structures with and without inclusion of intentional compensating deep impurity states as well as with and without epitaxial metal coatings.

GaAs/AlGaAs heterostructures containing high mobility two-dimensional electron gases just below the surface of a semiconductor were grown and provided to the Petta and Marcus group at Harvard for fabrication into two-electron double quantum dot systems. The structures were used to create and detect nuclear polarization by dynamic nuclear polarization and to probe and suppress statistical fluctuations in the nuclear spin bath and improve stability of quantum dot spin qubit systems. The double quantum dots were then used by Laird and Marcus to study electric dipole spin resonance and to make measurements of a two-electron spin qubit in a double quantum dot.

Similar structures containing high mobility two-dimensional electron gases just below the surface of the semiconductor were provided to the Amasha/Kastner group at MIT, where they were used to measure and control electron tunneling into the states of an empty lateral quantum dot in a magnetic field and for *in situ* electrical control of the spin relaxation rate of single electrons in the lateral quantum dots.

Among new epitaxial growths from UCSB that were sent to our Harvard NSEC collaborators in 2008 were 1) five samples of modulation doped GaAs/AlGaAs heterojunctions for imaging studies of near-surface two-dimensional electron gases by Erin Boyd in the Westervelt laboratory; 2) twelve GaAs/AlGaAs heterojunctions with various thicknesses, doping levels and aluminum contents for study of semiconductor band alignments by Dr. Wei Yi in Venky Narayanamurti's laboratory; 3) eight InGaAs quantum well structures for studies of tunneling by Kasey Russell in the Narayanamurti laboratory; and 4) three two-dimensional electron gas structures for study by Christian Barthel in the Charles Marcus laboratory.

Silica Nanowires for Microphotonic Devices

Eric Mazur

Applied Physics and Physics, Harvard University

Collaborators: Rafael Gattass (University of Maryland); Evgueni Slobodtchikov (Q-Peak, Inc.)

International Collaborators: Igor Khrushchev (Aston University, UK); Frank Marlow (Max-Planck-Institut für Kohlenforschung, Germany); Markus Pollnau (University of Twenty, Germany); Tetsuo Sakai (Keio University, Japan); Tobias Voss (University of Bremen, Germany)

Research Goal, Approach and Accomplishments

Silica nanowires provide strong mode confinement in a simple cylindrical silica-core/air-cladding geometry, representing a model system for the study of the nonlinear propagation of short pulses inside fibers. We observed supercontinuum generation by femtosecond laser pulses in silica fiber tapers of minimum diameters as small as 90 nm. This research was presented at the Photonics West 2006 Conference and was published in *Optics Express* **14**, 9408–9414 (2006).

Supercontinuum generation refers to extreme spectral broadening of a laser pulse propagating in a nonlinear material. Qualitatively, the degree of broadening of the supercontinuum spectra is understood in terms of the diameter-dependent dispersion and nonlinearity of the fiber. Contrary to supercontinuum generation by nanosecond pulses, for laser pulses propagating in negative dispersion regime, the observed spectrum is consistent with higher-order soliton formation and break-up. Because of the reduction of the interaction length to ~20 mm, and the low energy thresholds supercontinuum generation in tapered fibers is a viable solution for coherent white-light source in nanophotonics. Additionally, sub-200-nm diameter fibers possess negligible dispersion and nonlinearity making these fibers ideal media for propagation of intense, short pulses with minimal distortion.

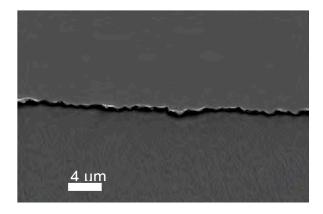


Figure 8.24. Scanning electron micrograph TiO_2 on a silica substrate. This preliminary investigation uses an etching recipe with SF_6 and Ar.

The low threshold energies required to generate supercontinuum indicate that microphotonic devices can be constructed that take advantage of these nonlinear effects. We also present a device based on the nonlinear Sagnac interferometer that permits optical switching and a number of all-optical logic operations with femtosecond laser pulses in the nanojoule range. The spectral broadening studied in the supercontinuum experiment reveals an optimal fiber diameter to enhance nonlinear effects with minimal dispersion. We fabricate Sagnac loops with lengths of about one millimeter from silica nanowires with diameters of 500–800 nm. Preliminary results show that we achieve light-on-light modulation. The data shows excellent agreement with predicted transmission behavior for a nonlinear Sagnac interferometer with a coupling parameter of 0.08. Our current research efforts are to increase the modulation depth of the transmission by controlling the coupling, and to significantly reduce the interaction length required for nonlinear phenomena.

Silica nanowires have also been used to efficiently launch light into ZnO nanowires. The optical properties of semiconductor nanowires are often characterized by using side-illumination. We can directly access the waveguide modes of the semiconducting nanowires by injecting light from tapered silica fibers. Initial results were presented at the Photonics West 2007 Conference and this work was published in *Nano Letters* 7 (12), 3675–3680 (2007).

We have investigated using the large evanescent field to sample a periodic substrate in order to create a Bragg mirror. By etching a substrate, a series of parallel troughs can be created forming a grating. When light propagates through a nanowire placed on top of this grating, the evanescent field will be exposed to alternating layers of substrate and air. This will produce a periodic effective index change, which acts like a dielectric mirror. Alternate configurations can also serve as a tunable frequency filter if the nanowire is rotated relative to the grating.

We have begun investigations into using TiO₂ as a novel nonlinear optics platform. The nonlinear index of refraction for TiO₂ is 140x10⁻¹⁹ m²/W (55 times greater than that of silica). Such high nonlinearities enable low light level nonlinear optics and efficient all-optical-switching. TiO₂ has a high index of refraction producing strong light confinement in addition to being CMOS compatible. Our preliminary work has been to take thin films of TiO₂ deposited onto silica then structure them using photolithographic techniques (Figure 8.24). Standard recipes for silicon and other materials are readily available, however these cannot be directly applied to TiO₂. Consequently, our research has focused on adapting and optimizing these recipes to make adaptable and scalable structuring in TiO₂ possible.

Intense femtosecond laser pulses can be absorbed in transparent materials and modify their refractive properties through nonlinear light-matter interactions. In glass, multiphoton absorption of femtosecond laser pulses leads to densification localized to the focal volume of the beam. Because the materials we pattern are transparent to the laser wavelength, the pulses can be focused at arbitrary points in the bulk or at the surface of the substrates. Thus, devices can be patterned in three dimensions using x-, y- and z-translation. This approach to material modification can be used in a variety of applications. We demonstrated the fabrication of three-dimensionally integrated optical components such as waveguides, splitters, couplers, interferometers and data storage

devices using this technique. We have made waveguides as long as 30 mm. (limited by sample size) and dots as small as 200 nm in diameter. For example, we demonstrated three-dimensional bulk optical data storage at 17 Gbits/cm³. Other groups have used the technique to fabricate a myriad of other types of devices, and entire conference sessions are devoted to femtosecond laser-based micromachining techniques.

The same fabrication principle can be used to fabricate freestanding structures. Our group has experience fabricating three-dimensional polymer structures with arbitrary shapes using two-photon absorption polymerization (Figure 8.25). We coat a substrate with a resin and photoinitiator mixture and then irradiate the viscous material with tightly focused femtosecond laser pulses. The resin contained within the focal volume of a pulse polymerizes via two-photon absorption in the photoinitiator. By controlling the position of the focus with a three-axis translation stage, we are able to fabricate complex polymeric microstructures in three dimensions.

We have recently begun applying the same technique to fabricate metal structures. Doping a bulk dielectric matrix with metal ions allows us to pattern metal structures through multi-photon induced metal reduction. This process is limited to a small volume where the laser is most intensely focused, which allows the fabrication of structures smaller than the diffraction limit of light. Figure 8.26 shows preliminary results we obtained depositing silver dots on glass substrates. Femtosecond laser based microfabrication is scalable and can be used to manufacture large volumes of micro- and nanostructures quickly and inexpensively. The femtosecond laser-based techniques can also be used to make three-dimensional electrical circuits, optical devices, and biological structures. The techniques provide the scalability and flexibility for rapid prototyping and large volume (cm³) manufacturing of three-dimensional nanostructured devices, offering several significant competitive advantages over conventional planar lithographic-based methods. We are investigating the technique with an aim to increase the resolution, repeatability and structure roughness through laser and chemical optimizations.

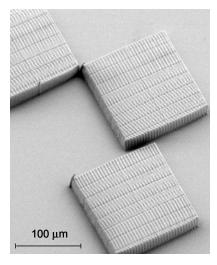


Figure 8.25. Scanning electron micrograph of femtosecond laser fabricated 3-D polymer structures.

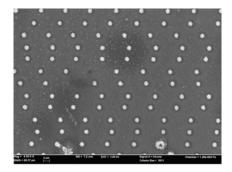


Figure 8.26. Scanning electron microscope image of laser-assisted silver deposition on glass substrate.

Synthesis and Characterization of Phase-Change Nanowire Heterostructures

Hongkun Park

Chemistry and Chemical Biology and Physics, Harvard University

Charge Separation Efficiency at a Nanowire-Polymer Heterojunction

Hybrid photovoltaic devices, composed of low-cost and solution-processable materials such as conjugated polymers and semiconductor nanocrystals, have garnered considerable attention as an inexpensive alternative to conventional solar cells for large-

scale solar energy conversion. Conventional solar cells achieve high power conversion efficiency by exploiting the long minority-carrier diffusion length of defect-free, and thus expensive, single-crystalline silicon. In a hybrid solar cell, the photo-generated electron-hole pairs are strongly bound and contribute to the photocurrent only if they manage to diffuse to the polymer/nanocrystal interface before recombination. Consequently, hybrid devices utilize only the majority carriers, and they do not require expensive single-crystalline materials.

Unfortunately, typical hybrid solar cells that have been realized to date are hampered by relatively low power conversion efficiency (< 5%). To improve the overall energy conversion, the better understanding of various intertwined processes. such photon absorption, exciton diffusion. charge separation, carrier transport and collection, is required. Most research in this area is carried out on ensemble devices consisting of bulk organic semiconductors mixed nanocrystals, where the performance of these devices is often convoluted by external parameters such as phase separation and component ratios.

In the grant period January 2008-January 2009, we characterized the photovoltaic effect of *p-n* junctions that consist of a single poly-3-hexylthiophene (P3HT) polymer strip and a single CdS nanowires (NW). Spatially resolved photocurrent imaging measurements reveal that the zero-bias photocurrent is observed only when the polymer/nanowire interface is illuminated. The current-voltage characteristics

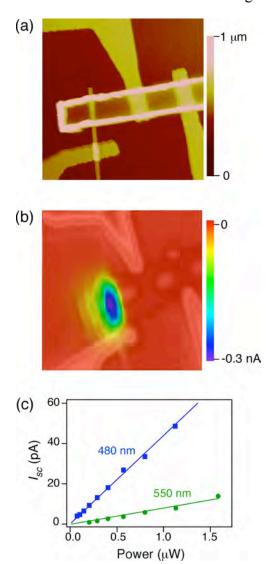


Figure 8.27. (a) AFM image of a typical heterojunction deice. The size of the image is 7×7 µm. (b) Overlap of the simultaneously taken reflection and photocurrent images of the same device. (c) Power dependence of I_{sc} at two different wavelengths.

under illumination can be understood using a simple equivalent circuit model that includes a light-induced charge leakage channel. With light-generated current at the junction decoupled from the external resistances, and interfacial exciton diffusion rate calculated based on device geometry, these planar devices allow estimation of the intrinsic charge separation efficiency as high 40% under laser irradiation with a wavelength of 532 nm. While the NW and polymer free carrier contributions vary dramatically below and above the band gap of CdS, the total separation efficiency is relatively flat over the entire spectral range of our experiment. The present study suggests that better interfacial engineering between the two components is critical to realizing high-efficiency hybrid solar-cell devices.

Self-assembled Quantum Nanostructures

Pierre M. Petroff

Materials, University of California at Santa Barbara

Collaborators: Craig Pryor (University of Iowa); Jelena Vuckovic (Stanford University)

International Collaborators: Per Olof Holtz (University of Linkoping, Sweden); David Gershoni (Technion, Haifa, Israel); K. Karrai (Ludwig Maximilian University, Munich, Germany); Richard Warburton (Heriot Watt University, UK)

Research Goals and Accomplishments

We have further developed the MBE growth of self-assembled InGaAs/GaAs quantum posts. These nanostructures consist of a short quantum wire terminated by a quantum dot at each end. When incorporated into heterostructures, the self-assembled quantum posts allows switching the electron from a 2-D to 3-D confinement regime with an applied field. We have explored a range of novel device applications.

Achievements

a) Quantum Posts Phase Mdulators:

We have shown the formation of giant electrostatic dipole moments in the InGaAs QPs and made use of these to demonstrate and enhanced electro-optics phase modulation in waveguides with InGaAs quantum posts. A phase modulation enhancement of 30% over that obtained with a quantum well device was indicative of a significant electro-optics coefficient with Quantum Posts [1].

b) Very Low Current Threshold Quantum Posts Oxide Aperture Vertical Surface Emitting Lasers:

We have fabricated oxide apertured vertical cavity surface emitting lasers (VCSEL) with quantum dots or Quantum Posts (QPs) in the active layer. The micropillar VCSELs have a $Q \approx 10,000$. The QPs VCSELs at low temperature showed a markedly lower threshold current (more than 100 times) than the QDs-based VCSELs [2]. The ultra-low current threshold-based devices suggest an increased modal gain and carrier collection efficiency of the QPs devices and we are currently modeling these effects .

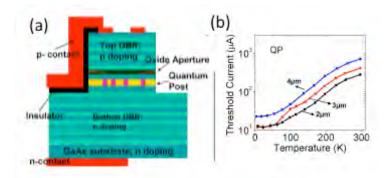


Figure 8.28. (a) Schematic of the oxide apertured VCSEL with a single layer of QPs in the gain medium region. Lasing threshold current as a function of temperature for different oxide aperture diameters.

c) A Tunable Quantum Post TeraHertz Absorber:

We have investigated the intrasubband absorption properties of quantum posts in the THz range and started the development of a THz quantum cascade laser. These devices make use of the field tunability of the intrasubband energy levels using the quantum wire size control and the quantum confined stark effect (QCSE). An absorption spectrum taken from a sample with 30 nm high QPs (open circles) and a sample with only a 30-nm wide InGaAs QW (full circles) are shown in Figure 8.31. While both curves show clear maxima at 3.4 THz and at 4.75 (4.6) THz, the QP spectrum exhibits a broad absorption lying underneath these two narrow resonances. Employing a correctly weighted fit to the QP data results in the solid black line that consists of two clear contributions from the QW like region surrounding the QPs (two red lines) and a broad absorption with a maximum at 5.2 THz (hatched blue area). Since this feature is entirely absent in the QW sample, we attribute this to the absorption directly in the QPs. The width of the absorption by the QPs is associated with their lateral size and shape distribution. We also observe a considerably larger absorption efficiency in the QPs sample and we are presently investigating the origin of this effect.

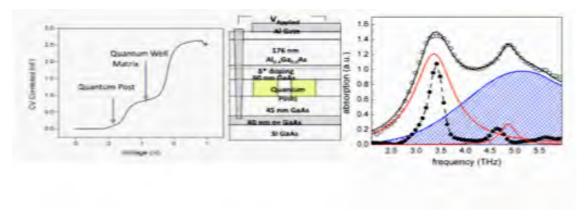


Figure 8.29. Device schematic used for loading the quantum posts with electrons using an applied voltage. The quantum post loading is detected by measuring the C-V characteristic of the device (*left*). The absorption spectra for a 30 nm quantum well (*filled circles*) and a 30 nm quantum post device (open circles) are shown at T = 10K. The shaded area is a deconvolution of the absorption spectra of the 2 spectra and corresponds to absorption of the quantum post layer.

We are currently modeling the absorption spectra as a function of the QPs dimensions and applied fields.

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Electronic and Structural Properties of High-quality VO₂ Thin Films

Shriram Ramanathan

Chemistry, Physics, Harvard University *Collaborator:* . K. Zawilski (BAE Systems)

Research Goal, Approach and Accomplishments

Goal is understand mechanisms governing phase transitions in vanadium oxide thin films and how they are affected by electric fields. Optical properties and valence band density of states near the Fermi level of high quality VO₂ thin films have been investigated by mid-infrared reflectometry and hard UV (hv = 150 eV) photoemission spectroscopy. Exceptionally large change in reflectance from 2 to 94% is found upon the thermally-driven metal-insulator transition (MIT). The infrared dispersion spectra of the reflectance across the MIT are presented and evidence for the percolative nature of the MIT is pointed out. The discrepancy between the MIT temperatures defined from the electrical and optical properties is found and its origin is discussed. The manifestation of the MIT is observed in the photoemission spectra of the V-3 d levels. The analysis of the changes of the V-3 d density of states is done and the top valence band shift upon MIT is measured to be 0.6eV.

CLUSTER 3: Imaging Electrons at the Nanoscale

Coordinator: Raymond Ashoori

Raymond Ashoori (Physics, MIT) Charles M. Marcus (Physics, Harvard)

Bertrand I. Halperin (Physics, Harvard)

Venky Narayanamurti (SEAS & Physics, Harvard)

Eric Heller (Chemistry&Physics, Harvard) Michael Stopa (NNIN, Harvard)

Jennifer Hoffman (Physics, Harvard) Robert Westervelt (SEAS & Physics, Harvard)

Marc Kastner (Physics, MIT) Amir Yacoby (Physics, Harvard)

Collaborators: M. Manfra, L. Pfeiffer, K.W. West (Lucent Technologies), R.D. Dupuis (Georgia Tech.)

International Collaborators: Fabio Beltram (NEST, Pisa, Italy), Leo Kouwenhoven (TU Delft, The Netherlands), Daniel Loss (University of Basel, Switzerland), Hiroyuki Sakaki (University of Tokyo, Japan), Lars Samuelson (Lund University, Sweden), and Seigo Tarucha (University of Tokyo and NTT, Japan)

Number of postdoctoral fellows: 2 Number of graduate students: 6 Number of undergraduate students: 3

Introduction

Electrons and photons inside nanoscale structures display striking behavior that arises from the confinement of quantum waves. By visualizing how electrons move through nanoscale systems, we can understand the fundamental science and develop new quantum devices. These devices can direct electron flow, or control the motion of electron charges and spins for nanoelectronics, spintronics, or quantum information processing.

Nanoscale structures are also promising for photonics: they can control the motion of optical waves using sub-wavelength devices. Near-field Scanning Optical Microscopy (NSOM) can be used to image and perturb these photonic systems.

The goal of the *Imaging at the Nanoscale* cluster is to develop new ways to image electrons and photons inside nanoscale systems, including their quantum behavior. This is difficult for electrons, because they are buried inside the structure, and because low temperatures are necessary. Nanoscale imaging of photonic systems also requires new approaches. This Cluster brings together a group of investigators who have designed and built scanning probe microscopes and developed new imaging techniques to image electrons and photons inside nanoscale systems. Close collaborations with theorists allow us to understand what the images mean.

Expected outcomes of this research are:

New Approaches to Imaging Electrons and Photons in Nanoscale Systems — Custom-made scanning probe microscopes coupled with theoretical analysis allow us to understand the quantum behavior of electrons and photons inside nanoscale systems. These techniques are based on cooled Scanning Probe Microscopes (SPMs) capacitively coupled to the electrons below, Magnetic Force Microscopes (MFMs), Scanning Tunneling Microscopes (STMs), Ballistic Electron Emission Microscopy (BEEM), and Electron Emission Luminescence (BEEL) Microscopy. Near-field Scanning Optical

Microscopy (NSOM) using custom tips can be used to investigate photonic systems. The investigators are experts in the design and fabrication of scanning probe microscopes.

New Nanoelectronic and Photonic Devices — Visualizing the motion of electrons and photons in nanostructures allows us to develop new types of nanoelectronic and photonic devices and systems, based on nanocrystals and nanowires from the Nanoscale Building Blocks Cluster, and on semiconductor heterostructures grown at the MBE Lab at UC Santa Barbara. These new materials offer exciting opportunities. Imaging and theoretical simulations will allow us to design new devices and understand how they work.

Physics of Graphene Sheets

Raymond Ashoori

Physics, Massachusetts Institute of Technology

Collaborators: Jak Chakhalian (Univ. of Arkansas); Jing Kong (Massachusets Institute of Technology); Pierre Petroff (Univ. of Calif., Santa Barbara); Loren Pfeiffer (Bell Labs/Alcatel-Lucent Technologies)

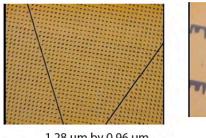
International Collaborator: Jochen Mannhart (Augsburg University, Germany)

Imaging of Graphene Sheets

We have been working to perform our charge accumulation imaging on the graphene sheets. Compared to our previous experiments on buried 2-D systems, we expect to achieve significantly higher spatial resolution in graphene because the scanning tip can be moved up directly against the surface. Moreover, we will be able to perform direct STM imaging along with our capacitance techniques. We note though that capacitance has an important feature lacking in STM. In STM, the bias set between the tip and the sample controls the tunneling current and cannot be adjusted independently of the tunneling current. Therefore, even at small biases one often ends up with large electric fields between the tip and the sample due to workfunction differences. In capacitance, there is no tunneling current, and we can adjust (and null) at will the electric field between the tip and sample and thereby control the perturbation created by the tip. Finally, having the tip so close to the sample will allow for very high resolution scanned gate measurements.

We plan to perform the same types of scanning bubble experiments on graphene in the quantum Hall effect regime as we have done in GaAs. This will give us a good idea of the types of short-range disorder that exist in these structures. Later experiments may examine high current saturation in the material (as occurs in nanotubes) and conducting pathways. This is perhaps the most exciting new electronic materials systems to arise in the last decade.

Part of the difficulty in performing our scanning experiments on graphene involves finding the sheet of graphene. We have created search patterns (shown in Figure 8.30) and can image marks that will guide us to the location of a small piece of graphene.



1.28 um by 0.96 um optical microscope image



128 um by 96 um optical microscope image



12 μm x 19 μm scanning capacitance image

Figure 8.30. Search patterns for finding a small piece of graphene on a surface with a scanning capacitance tip. Our capacitance microscope can detect the marks (right) and then walk to the small ($\sim 10 \times 10$ micron) piece of graphene.

As we had some difficulty with the coarse movement in our microscope, we decided to take a quicker route to taking measurements on graphene. The group of Prof. Jing Kong at MIT has devised a novel CVD method for growing large sheets of graphene. These sheets are several millimeters on a side, and they are big enough so that it is easy to find them with our capacitance microscope. We have succeeded in producing images from these samples, but we have not yet managed to perform bubble imaging.

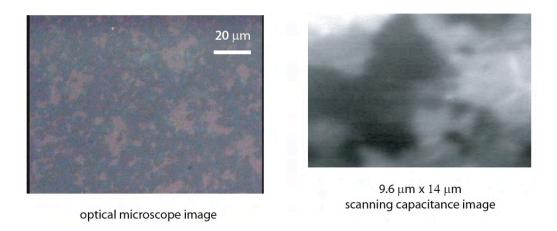


Figure 8.31. – *Left* shows an optical image of a large piece of CVD graphene. *Right* shows an image from our capacitance microscope. The capacitance microscope is sensitive to structure observed optically.

Theory of Electron and Spin Transport in Nanostructures

Bertrand I. Halperin

Physics, Harvard University

Collaborators: Karen Le Hur (Yale University), Leonid Levitov (MIT), Chetan Nayak (Microsoft Corporation), Loren Pfeiffer (Alcatel-Lucent), Pabitra Sen and David Johnson (Schlumberger), Kun Yang (Florida State University); Robert M. Westervelt, Charles M. Marcus, Amir Yacoby (Harvard University)

International Collaborators: Ian Affleck (University of Britisch Columbia, Canada) Leo Kouwenhoven (Delft University of Technology), Jiang Qian (Ludwig-Maximilians University, Munich, Germany), Bernd Rosenow (Max Planck Institute), Ady Stern (Weizman Institute, Israel)

Research Goal, Approach and Accomplishments

The overall goal of this work is to gain a better understanding of the electronic structure of nanoscale building blocks, and of the operations of nanoscale devices, in order to improve our ability to design and construct such devices. A crucial aspect of the development of new structures and devices are measurements to characterize these structures. Theoretical efforts are necessary to understand the results of such measurements as well as to suggest new types of measurements as well as possible improved structures. Our projects are motivated by NSEC supported experiments including particularly measurements of transport in semiconducting nanowires, and imaging of electron flow and electronic states in structures made from nanowires or two-dimensional electron systems. Goals include development of theoretical and calculational techniques, as well as applications to specific systems.

Nanowires. InAs nanowires are a particularly interesting system for fabrication of nanoscale semiconductor devices, and they are being actively studied in laboratories of the <u>Westervelt</u> and the Kouwenhoven groups, among others [1]. We are trying to understand the electronic states in these wires, and trying to see how much information one may gain by analyzing transport in the presence of an inhomogeneous gate potential. We are also interested in effects of an applied magnetic field. Electron-electron interactions play a central role in our analyses.

In 2008, motivated by experiments in <u>R.M. Westervelt's</u> laboratory, we performed theoretical investigations of ways in which a charged scanning probe could be used to manipulate electrons and to study the electronic states of a few-electron quantum dot in a thin InAs nanowire. Calculations were carried out by a postdoctoral fellow, Jiang Qian, under the supervision of <u>B.I. Halperin</u> and <u>E.J. Heller</u>. Results were reported in a manuscript entitled "Imaging and manipulating electrons in a one-dimensional quantum dot with Coulomb blockade microscopy," which has been posted on the web and submitted for publication [2].

In the experimental setup, a quantum dot was formed in a segment of InAs nanowire, by means of two short barrier segments, made from InP [1,3,4]. The nanowire was placed on a substrate consisting of an insulating two-dimensional SiO_x layer, on top of a highly doped silicon substrate, and leads were attached to the ends of the nanowire. A negatively charged probe tip was scanned above the wire, while conductance through the

wire was monitored. In our analysis, we considered particularly the case where the nanowire is thin enough that all electrons are in the lowest transverse quantum mode, and the InP barriers are thick enough so that transport is in the Coulomb blockade regime. Conductance peaks occur when the energy of the dot with N electrons is degenerate with the case of N-1 electrons. Experimental information about these energies is obtained by monitoring the way in which the peak positions change, as a function of the charge, position, and height of the probe tip, as well as of the chemical potential, which can be controlled by applying voltage to the Si substrate. (See sketch in Figure 8.32)

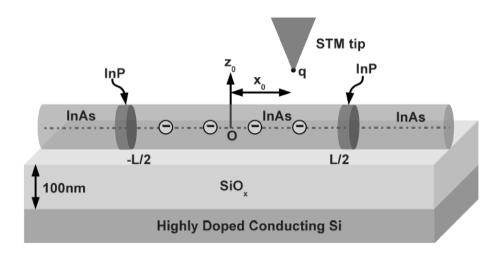


Figure 8.32. Schematic geometry for Coulomb blockade microscopy of a nanowire containing four electrons.

The theoretical analysis used a model in which electrons were confined to move in one dimension, but the interaction between them and their interaction with the probe tip was calculated in a three-dimensional model, taking into account the SiO_x dielectric layer as well as the metallic Si substrate. The electronic ground state energy was calculated by exact diagonalization of the quantum-mechanical Hamiltonian, including the spin degree of freedom, for up to four electrons in the dot.

For small magnitudes of the tip voltage, the effect of the tip can be treated as a small perturbation, and computed shifts in Coulomb blockade peaks can be interpreted as a measurement of the electron density in the unperturbed ground state. For a sufficiently long wire segment, where the electron Coulomb repulsion dominates the kinetic energy, the electron density should be Wigner-crystal-like, with the number of maxima equal to the number of electrons in the wire. For shorter wires, where the kinetic energy dominates, the density profile should be more like that of non-interacting electrons. Here the density shows Friedel-like oscillations, where, if the number of electrons is even, the number of peaks is just half the number of electrons. (In Hartee-Fock [5], we would say that spin-symmetry is preserved in this regime; the reflecting boundaries produce the same density modulation for both spin states, with a wave vector equal to $2k_F$.) Both of these regimes are observed in our calculations, with a transition between them for a wire length of roughly 150 nm, for a wire of radius R = 10 nm.

For large tip voltages, the situation is quite different as the probe can have a major effect on the electrons in the wire. If the voltage is sufficiently large, and the tip is sufficiently close, the electron density may be suppressed to near zero under the tip, effectively dividing the wire into two separate segments. For example, if there are four electrons in the wire, they may be divided (2,2), if the tip position is near the center of the wire, or (3,1) or (4,0) if the tip is close to one end of the wire. As the tip position is changed there can be a rather abrupt transition, where an electron moves from one end of the wire to the other, accompanied by a discontinuity in slope in a plot of the ground state energy vs. tip position. Such discontinuities would be manifest in the shifts of Coulomb-blockade peaks. (See Figure 8.33) The positions of these discontinuities will be affected by electron-electron interactions within the wire.

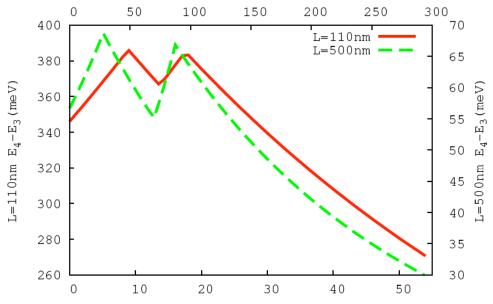


Figure 8.33. Energy difference between ground states of N=4 and N=3 electrons, as a function of probe position x_0 , for wire lengths 110 nm and 500 nm. Tip is 30 nm above the wire's center axis, and tip charge of 24 electrons is in the strong tip limit.

Spin-orbit effects. Spin-orbit effects on transport in semiconductor systems have been a major focus of interest over a period of years, as analysis has shown a remarkable subtlety in these problems. The work supported by NSEC has concentrated on effects of confinement in small quantum dots and phenomena at a boundary or interface between 2D regions with different spin-orbit coupling. In 2008, graduate student Jacob Krich, working with <u>B.I. Halperin</u>, completed an analysis of the statistical distribution of spin-polarization expected in a the exit current from a chaotic quantum dot, produced by spin orbit coupling from an unpolarized entering current, in the absence of a magnetic field. Random matrix theory was used to calculate typical polarizations, as a function of the number of channels in each lead, in the limit of strong spin-orbit mixing [6].

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Physics of Scanning-Probe Microscope Imaging of Nanoscale Systems

Eric Heller

Chemistry, Physics, Harvard University

Collaborators: Don Eigler (IBM Almaden); Lev Kaplan (Tulane University); Hari

Manoharan (Stanford University), R.M. Westervelt (Harvard)

International Collaborators: Tobias Kramer (University of Regensburg, Germany); Chi-Te Liang (National Taiwan University)

From January 15, 2008–January 14, 2009, several lines of research were pursued. These fall into four categories: (1) Electrons and electron imaging in quantum wires, (2) new theoretical approaches to quantum Hall physics, (3) new approaches to graphene scattering and conductance in realistic geometries with defects present.

1. Electrons and Electron Imaging in Quantum Wires

Quantum wires are under intense study as possible future useful devices and as laboratoires for fundamental studies of electron transport and correlations. Of particular interest is the imaging and control of the electrons in the wire by means of a charged scanning tunneling microscope tip. In collaboration with R.M. Westervelt and his group, and with B.I. Halperin and a shared postdoc, Jian Qian, we have begun a very promising line of investigation featuring explicit calculations of conductance as a function of tip position near a InAs naowire. Following on successful early experiments in the Westervelt group, Jian Qian, a postdoctoral fellow in the Heller group and former student of Professor B.I. Halperin, completed explicit four electron calculations using a full and realistic Hamiltonian, including screening of the full Coulomb potential, the presence of a movable charged scanning probe microscope tip, etc. It was found that the resulting conductance signal revealed two important regimes, including evidence for one electron jumping across the repulsive barrier provided by the SPM tip potential. This has led to the 2008 submission of a manuscript, "Imaging and manipulating electrons in a onedimensional quantum dot with Coulomb blockade microscopy," also available on the web Archive.

- **2.** By using our recently developed time-dependent FFT wave-packet technology, which makes explicit calculations on a given background potential, impurity field, electric field gradient, and magnetic field under thermal averaging possible for the first time, we have been able to reproduce the integer Quantum Hall plateaus quantitatively for the first time, including new plateaus seen for the first time at higher electric field gradients. This has resulted in a paper submitted to *Nature Physics*, also available on the web Archive. The same technology was applied to the transconductance of a two-quantum point contact device in the presence of a strong magnetic field, in a 2008 paper, "An efficient and accurate method to obtain the energy-dependent Green function for general potentials," published in the *Jounal of Physics*.
- **3.** We have developed a new approach to Quantum Hall problems, which was used as the underpinning of the wave-packet calculations mentioned in (2), involving an injection

model for the electrons. It is known that the corners of a quantum Hall bar are sites for the injection of electrons, and that dissipation happens there, as evidenced by the heat released at the corners. We realized that if the electron injection histories could be computed the problem of the off-diagonal resistivity plateaus might be calculated; we found that this was the case, and for the first time ever in the field. The same ideas were used to predict the conductance properties of a graphene Hall bar, with equally good results, at both lower and moderate magnetic fields, where the experimental undulations are well reproduced. The philosophy here is much like that of QPCs in a two-degree freedom electron gas: Understand the flux at the injection point, and you understand the conductance. This has resulted in a paper submitted to *Physical Review Letters*, also available on the web Archive.

High Spatial Resolution Magnetic and Electrostatic Force Microscope

Jennifer Hoffman

Physics, Harvard University

Collaborators: Chang-Bum Eom (University of Wisconsin, Madison); Alex de Lozanne (University of Texas, Austin); Ralph Weissleder (Massachusetts General Hospital)

Research Goal, Approach and Accomplishments

The goal of this project is to detect and measure both magnetic and electrostatic forces with sub-nanometer spatial resolution and sub-picoNewton force resolution by employing both a vertical and horizontal cantilever, coupled with AC magnetometry. This novel imaging technology has many potential uses. Some initial systems we may study include:

- 1. Magnetic nanoparticles, via magnetic force microscopy
- 2. Vortices in high temperature superconductors, via magnetic force microscopy
- 3. Multiferroics, via both magnetic force microscopy and kelvin force microscopy

Magnetic Nanoparticles (Fe₃O₄)

Magnetic nanoparticles have many potential uses, including:

- Nanomagnets for the future information storage due to their high spatial density
- Magnetic nanoparticles for medical diagnostic and therapeutic technology

Much attention has recently been paid to magnetic nanoparticles for the biological application such as targeted cancer treatment, guided drug delivery, and magnetic MRI. The understanding of magnetic nanoparticles is challenging at the nanoscale. The current resolution of magnetic force microscopy (MFM) is around 20 nm, which is not sufficient for imaging magnetic nanoparticles with a size of 10 nm or less. We have been developing cantilever-based AC magnetometry in order to push the MFM resolution of as low as 10 nm. Dr. Ralph Weissleder's group at Mass General Hospital is working to optimize the size and composition of magnetic particles (Fe₃O₄) for NMR and MRI applications. Specifically, they aim at developing superparamagnetic particles with a nanometer size (around 10 nm), excellent buoyancy and extremely high magnetization. Magnetic particles are coated with an antiferromagnetic layer to avoid agglomeration. They found an abnormal hysteresis curve that is not explained with a conventional theory. A high-resolution magnetic imaging technique is needed to understand the abnormal hysteresis.

We plan to use our new magnetic force microscope with a novel AC technique to probe magnetic domains of those particles. We have developed a technique for the preparation of Fe₃O₄ particles on a Si wafer. Unlike gold nanoparticles, Fe₃O₄ particles are hydrophobic; these are not stable on a hydrophilic surface as a Si wafer.

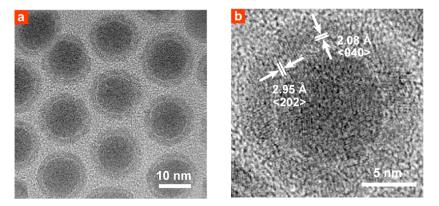


Figure 8.34. TEM images of Fe₃O₄ nanoparticles. (a) Fe₃O₄ nanoparticles coated with FeMn. (b) TEM image of a single Fe₃O₄ particle. (Figure courtesy of Dr. Hakho Lee)

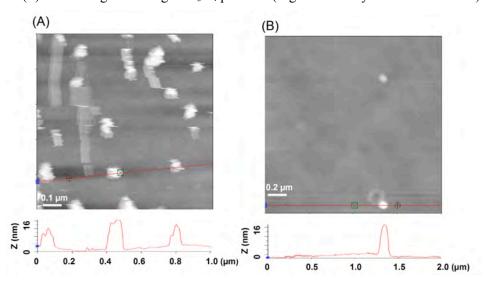


Figure 8.35. AFM images of Fe_3O_4 nanoparticles taken in the hydrophilic (**A**) and hydrophobic (**B**) surface. (Images are taken with the asylum AFM in CNS.) Iron nanoparticles are hydrophobic. Therefore, the friction between iron nanoparticles and hydrophilic Si surface (**A**) is less than that between those nanoparticles and hydrophobic surface (**B**). Individual nanoparticles are wiggling around and a few show ghost images, which reflects particles moving while scanning. HMDS (hexamethyldisilazane) was used to turn a hydrophilic Si surface into a hydrophobic Si surface, to stabilize the particles.

Multiferroics (BiFeO₃)

Multiferroics, materials that have coupled electric, magnetic, and structural order parameters, have attracted considerable attention due to their fundamental interest and the exciting application potential in next generation data storage, since the gigantic magnetoelectric (ME) effect in the multiferroic TbMnO₃ was discovered. Manipulation of magnetization by electric fields has become an important technical challenge. The capability of addressing magnetic domains with electric fields in multiferroics will lead to faster and more compact devices in hard disk manufacturing.

BiFeO₃ (BFO) is a room-temperature multiferroic that has a large electrical polarization. However, the microscopic coupling mechanism between magnetic domains and electric polarization domains is elusive due to the domain size of a few nanometers that is not accessible with conventional magnetic imaging techniques. Our microscopy will be ideally suited to study this new class of a multiferroic material, as we have the capability to probe both the magnetic and electric domains simultaneously with the novel AC magnetometry technique.

Superconducting Vortices

Though applied research has been carried out in superconductors, little is known about the microscopic motion and pinning of single vortices. Our magnetic force microscope employs a vertical cantilever capable of manipulating single vortices and measuring directly lateral pinning forces. The vertical cantilever also allows higher force sensitivity, by solving the 'snap-in' problem associated with ultra-soft high sensitivity cantilevers.

Instrument Construction

Undergraduate Stanley Chiang designed the MFM table. Postdoctoral Fellow Dr. Martin Zech built the MFM table. Undergraduate Hamsa Srihhar measured mechanical noises by vertical and horizontal geophones. Graduate student Tess Williams fabricated vertical cantilever tips with high aspect ratio and small radius of curvature. Postdoctoral Fellow Dr. Jeehoon Kim, the MFM project leader, rewired the cryostat, built the fiber interferometer system, and tested a vertical cantilever in vacuum. The quality factor (Q) of 150,000 was observed in vacuum with a vertical Si cantilever. In order to reduce a Q value without sacrificing a-signal-to-noise ratio, Dr. Kim developed an active Q control system employing a phase shifter. The active Q control system will allow us to drive a cantilever amplitude of less than 1 Å, which is essential for a vertical cantilever to achieve a high spatial resolution. Another active Q-control system using radiation pressure is under development for Kelvin force microscopy.

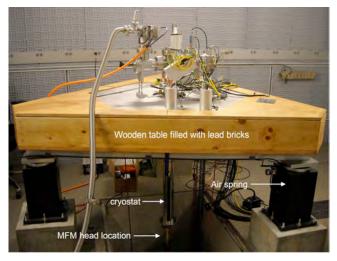


Figure 8.36. The magnetic force microscope construction has been completed, and some parts machined by the Harvard shop in the Engineering Sciences Laboratory. The wooden table is filled with 2100 pounds of lead bricks for the isolation of low frequency mechanical noises.

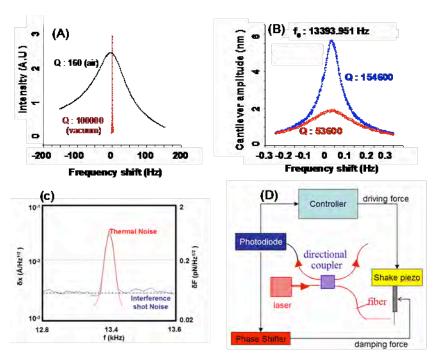


Figure 8.37. (A) The cantilever quality factor Q test under the pressure of 1×10^{-7} Torr. The quality factor Q in vacuum increased by three orders of magnitude. (B) To decrease a quality factor, without sacrificing the signal to noise ratio, an active Q control method was used. (C) Interference shot noise level. (D) Schematic of the active Q system, showing phase shifter and capacitive coupling.

Imaging Spins in Quantum Dots

Marc A. Kastner

Physics, Massachusetts Institute of Technology

Collaborators: Arthur C. Gossard (University of California at Santa Barbara); Charles M. Marcus, Robert M. Westervelt (Harvard University); Loren Pfeiffer (Bell Labs/Alcatel-Lucent Technologies); Ya-Hong Xie (University of California at Los Angeles)

Research Goal, Approach and Accomplishments

The long-range goal of our NSEC work is to image electron spins in quantum dots. Westervelt's group has made great advances in imaging electron charge density. Imaging the spin density of electrons in nanostructures will give additional information about electronic wavefunctions and may be useful in characterizing devices, for quantum computing for example.

This year our work related to this goal focused on the fabrication of quantum dots in Si quantum wells. The attraction of Si, compared to GaAs, is that the decoherence caused by nuclear spins could be much reduced. First, the fraction of nuclei in Si that have spins is much smaller than in GaAs, although this effect goes only as the square root of density. Second, and much more important, the hyperfine coupling between the nuclear and electronic spins is much weaker for lighter atoms.

We have heterostructures containing Si quantum wells on strained-layer SiGe substrates grown by molecular beam epitaxy by Ya-Hong Xie at UCLA. An electron micrograph of one of the electrode structures created on these substrates are shown in the figure below.

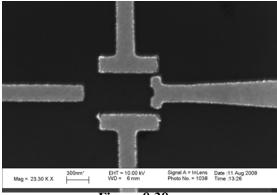


Figure 8.38

We have encountered various problems that have prevented us from creating controlled dots. First, we had to overcome leakage between electrodes and the two-dimensional electron gas in the Si quantum well. We followed the approach of the Erikson group and made the area under the electrodes small, by narrowing the mesa, and this eliminated the leakage. Second, we found that large negative voltages

were needed to deplete the 2DEG under the electrodes. We hypothesized that this was because of large variations in electron density resulting from strain in the SiGe. Our samples show a "plaid" pattern in AFM images (see the figure below), suggesting a strain pattern on the scale of micrometers, and this strain could cause density variations. We have eliminated this problem by using a plasma etch step before the metal is deposted for the nanometer electrodes. We believe that the additional surface states caused by the etching depletes the 2DEG. Unfortunately, even these devices show no controlled dot behavior. From discussions with Mark Erikson we believe that this may be a result of

conduction in the doped layer, so we have obtained heterostructures with various doping levels, to try to eliminate this conduction. We have fabricated dots on these and are beginning to test them. We are hopeful that this year will yield controlled dots, and that we will be able to carry out spin resonance measurements on these.

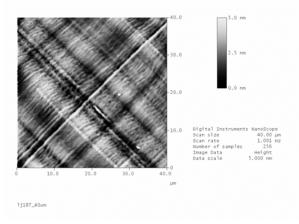


Figure 8.39.

Nanoparticle-Based Molecular Imaging via MRI

Charles M. Marcus

Physics, and Center for Nanoscale Systems, Harvard University

Collaborators: Carol Lynn Alpert (Museum of Science); David Cory (MIT), Gloria Hoefler (Agilent Technologies); Susan Kauzlarich (University of California, Davis); Zhifen Ren (Boston College); Bruce Rosen (Massachusetts General Hospital

International Collaborator: Sandro Erni (University of Basel, Switzerland)

Research Goal, Approach and Accomplishments

Silicon-based nanoparticles offer promise as biologically targeted magnetic resonance imaging (MRI) agents based on their exceptional nuclear magnetic resonance (NMR) properties, lack of background signal and diverse functionalization chemistry. Specifically, the long room temperature nuclear relaxation (T_1) times makes them suitable candidates as *ex vivo* polarized imaging agents, as they can be transported and administered on practical time scales without significant loss of polarization. We have studied the room temperature NMR properties of both commercially synthesized and ball-milled silicon nanoparticles (Figure 8.40a) at 2.9 T and find that T_1 depends on particle size, dopant concentration and morphology. We have also investigated the polarization enhancement of these particles using microwave-induced dynamic nuclear polarization (DNP). DNP experiments were performed at 4 K in a 2.9 T superconducting NMR magnet ($f_{NMR} = 24.4$ MHz, $f_{ESR} = 81$ GHz). This work was done by graduate student Maja Cassidy, working with Harvard undergraduate, Chinh Vo, NNIN-REU summer student Daniel Reeves, and high school student Samuel Rodriques.

A custom built cryostat and insert with a vertical saddle coil probe allows for rapid loading and unloading (< 5 s) of the hyperpolarized sample without disturbing the cryogenic setup. Figure 8.40 shows a single-shot NMR spectrum of 50 nm diameter particles polarized at 4 K for 4 hours. This represents a polarization enhancement of 1000 over the thermal equilibrium spectrum (Figure 8.40c).

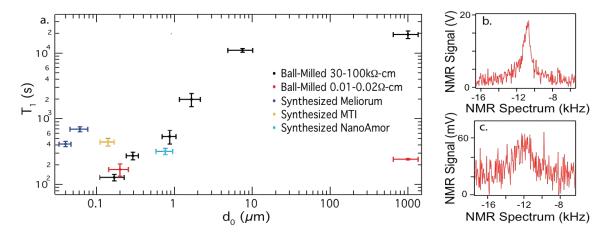


Figure 8.40. (a) Room temperature nuclear T₁ times vs particle diameter of silicon nanoparticles. (b) Single-shot NMR spectra from 50 nm silicon nanoparticles polarized via DNP at 4K. (c) NMR spectrum of 50 nm silicon nanoparticles at thermal equilibrium.

An important feature of hyperpolarized MRI is that large fields are not needed for imaging because the hyperpolarized agent carries a large nuclear polarization independent of the applied field magnitude. To exploit this feature, we have pursued the construction of a low-field MRI system. During the past year, coils for nuclear magnetic resonance (NMR) were built and gradient coils for MRI were designed, built, and assembled by Sandro Erni, a visiting student from University of Basel (an NSEC partner), along with two Harvard undergraduates affiliated with the project and one high school student from a local high school. The whole system was set up, and first tests were done to prove its operational capability. The MRI system is shown in Figure 8.41. Proton NMR was proved to work on water samples at magnetic fields between 18 mT and 30 mT. Tests also showed that the MRI gradient coils are working as expected and are adequate for imaging.

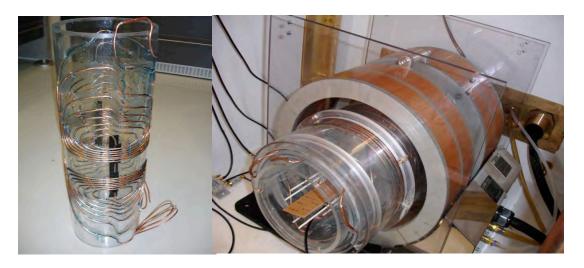


Figure 8.41. MRI gradient coil design of one of the three coils (*left*) and the assembled imaging system including main electromagnet, MRI gradient coils and NMR coils (*right*).

Photonic Devices Based on GaN Nanowires

Venkatesh Narayanamurti

Applied Physics and Physics, Harvard University

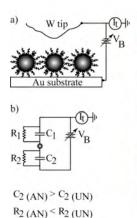
Collaborators: S. Ramanathan (Harvard University); M. Bawendi, V. Bulovich (Massachusetts of Technology); K.Y. Cheng (University of Illinois); R.D. Dupuis (Georgia Tech.); Arthur Gossard (University of California, Santa Barbara); L.R. Ram Mohan (Worcester Polytech Institute); G. Seryogin (Liminus, Inc.); A. Shakour (University of California, Santa Cruz)

Research Goal, Approach and Accomplishments

In the past year substantial progress was made in using the dual tip STM to study colloidal quantum dots in collaboration with Professors Bulovich and <u>Bawendi</u> at MIT. The results are summarized in Part A below. The work on GaN nanowires led to the first observation of dielectric confinement and the dependence of donor activation on wire radius. See section B. In addition working with Professor <u>Capasso</u> the scalable fabrication of nanowires photonics and electronic circuits using spin-on glass was accomplished. Finally, great progress was made in a joint project with Professor <u>Ramanathan</u> on understanding transport in VO₂ thin films. See section C.

A. Scanning Tunneling Microscope Studies of Charge Injection in Colloidal Quantum Dots

Since last Spring, graduate student Marissa Olson-Hummon and postdoctoral associate Andrew Stollenwerk have developed several experimental techniques that probe charge injection and retention of colloidal quantum dots. Our first objective was to repeat scanning tunneling microscopy (STM) experiments on known CdSe core quantum dots. We observed a characteristic increase in zero conductance region (ZCR), a measurement of the band gap of the semiconductor plus the electron-hole Coulomb, with a decrease in the size of the quantum dots. We are currently pursuing probing the charging energy of annealed core/shell, CdSe/ZnS, quantum dots. These dots formed a submonolayer on template stripped gold and were annealed to reduce the contact potential between the dots and the surface by removing some of the ligands.



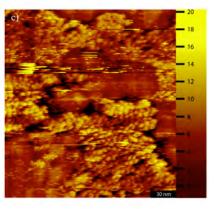


Figure 8.42. Tip-QD Schematic (a), equivalent circuit modeling the double barrier tunnel junction (b), and STM image of CdSe/ZnS colloidal quantum dots on template stripped Au substrate at Vsub = 2.5 V and Inset = 200 pA (c).

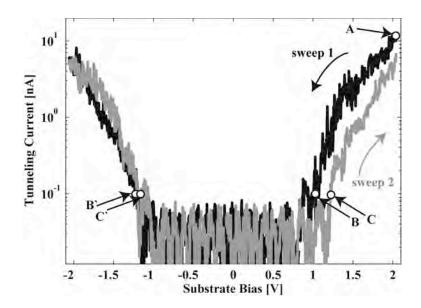


Figure 8.43. I-V hysteresis due to trapped charges. The potential difference between points B and C (marking the conduction band edge) is the Coulomb blockade.

Tunneling spectra are taken in sequential pairs, first a decreasing bias sweep, immediately followed by an increasing bias sweep, as shown in Figure 8.43. Before each set of spectra is collected, the feedback loop of the STM is closed for 1.0 s to ensure the tip height above the QD is constant between sets of spectra. The feedback loop is then opened and the bias is set to the first data point and held there for either 0.0 s or 0.25 s. We analyze each set of spectra to determine the extent of the shift in the conduction (valence) band edge by comparing points **B** and **C** (**B**` and **C**`) in Figure 8.44. The difference between **B** and **C** is the Coulomb blockade (CB) and is a measure of the decrease in conductivity due to charge(s) trapped on the QD. We determine the discharge potential, the bias applied to the substrate to remove a charge from the QD, from the IV curves by taking the largest bias of the first sweep, most often, the starting point of the IV curve (point **A** in Fig. 8.43).

Figure 8.45 shows the Coulomb blockade for positive discharge potentials, corresponding to shifts measured on the conduction band edge. The wait of either 0 or 250 ms and the tip stabilization always occurred at a positive bias. The weighted average of the 250 ms data shows a shift from 5 meV to 69 meV at a discharge potential of \sim 1.6 V. The 0 s data, however, shows a consistent average CB of 11 meV. We measure the charging energy for the dot as the difference in potential between the steps on the 250 ms measurements, approximately 65 meV.

We model our quantum dot core as a sphere of radius 2.1 nm with a dielectric constant of 8. The trapped charge is most likely located on the surface of the core at the site of a dangling Se⁺ bond. We assume it has some capacitance to the surface and its nearest neighbor QDs mitigated by the ZnS shell and aliphatic ligands. Our measured charging energy of 65 meV is close to the calculated charging energy, $E_C = e^2/(2C)$, if the ligands have a length of ~0.8 nm and a dot-to-dot separation (measured from center to center) of 6.8 nm.

Future Experiments

There are several avenues we would like to explore regarding quantum dot charging. It would be very valuable to have a better understanding of the dot-substrate contact. We are currently developing a method of quantitatively contrasting the capacitance between

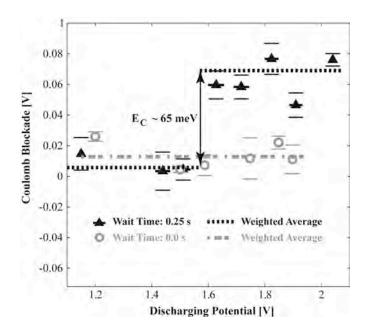


Figure 8.44. Coulomb blockade as a function of discharge potential. We see a distinct jump in the measured Coulomb blockade at ~1.6 V, from 4 meV to 69 meV (weighted averages), which is the charging energy for the quantum dot.

the dot and substrate for different ligand coatings and different charge states ($N_e = 0$ or $N_e = 1$). We would also like to model the barrier shape, as well as the trap depth, by carefully evaluating the lifetime of the trap state under various substrate bias conditions. We plan to contrast our measurements on the annealed dots to unannealed dots that presumably have a wider barrier. We may be able to determine if the ligands play a role in charge transport or if the carriers simply tunnel through the ligand region.

B. Size-Dependent Impurity Activation Energy in GaN Nanowires

The effect of the surrounding dielectric on the conductivity of GaN nanowires is measured experimentally. Extraction of the activation energy from the conductivity demonstrates, for the first time, the effect of dielectric confinement on impurity activation. Two configurations are considered; bare, suspended and SiO₂-coated nanowires. See Figure 8.45. The measured conductivity is consistently fitted by two exponential terms with different activation energies, indicating multi-channel conduction. The larger energy, attributed to activation of impurities into the conduction subband, shows essentially inverse dependence on nanowire radius, arising from dielectric confinement. This agrees with calculated values from finite element analysis. See Figure 3.46. The smaller energy is independent of the nanowire radius, suggesting a surface conduction channel.

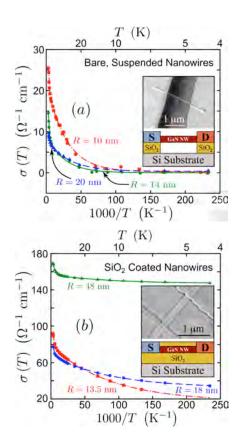
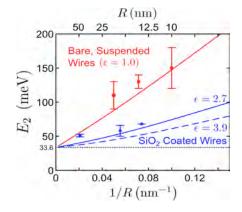


Figure 8.45. The experimentally measured conductivity (points) and the fits to Eq. (1) (curves) for (a) bare, suspended GaN nanowires with 10, 14, and 20 nm radii, and for (b) SiO₂-coated GaN nanowires with 13.5, 18, and 48 nm radii. Each inset shows an SEM image and schematic representation of the dielectric configuration.

Figure 8.46. The activation energies E_2 (points) from fitting $\sigma(T)$ with Eq. (1) for each nanowire versus the inverse wire radius, with the error in each energy. The curves are from finite-element method calculations. The FEM calculations were done with SiO₂ dielectric constants of 2.7 and 3.9 for comparison, as the coating was not thermally grown and hence could have a dielectric constant different from that of bulk SiO₂.



C. Study of Structure-Property Relationship in VO₂

Rf-sputtered VO₂ films grown in Professor <u>Ramanathan</u>'s laboratory have been studied by a joint postdoc (D. Ruzmetov). The work this year has led to correlation of the X-ray absorption spectroscopy measurements with the transport properties as a function of temperature and the metal—insulator transition. Hall measurements show for the first time the enormous change in electron carrier density at the transition temperature. The results are consistent with the electron-electron correlations and a Mott-Hubbard type transition.

Simulations of Electrons in Nanowires and Coupled Quantum Dots

Michael Stopa

Center for Nanoscale Systems, Harvard University

Collaborator: Normand Modine (Sandia National Laboratory)

International Collaborators: Toshi Iitaka (Riken, Kobe, Japan); Seigo Tarucha (University of Tokyo)

(University of Tokyo)

Research Goal, Approach and Accomplishments

Nanowires

Goals

(i) Calculate the electronic structure, within the effective mass approximation, for semiconductor nanowires in a realistic environment, i.e., consider the ambient leads, gates and, where appropriate, metallic tips of scanning probe microscopes. For isolated regions of these wires, where quantum dots are formed, calculate the total energy and Kohn-Sham eigenstates for fixed charge states and sets of gate voltages.



Figure 8.47. Schematic of semiconductor nanowire with scanning

(ii) Determine the electronic structure for nanowires made of varying materials where lattice mismatch can produce strain fields. In particular, for silicon-germanium wires, employ the strain field calculated from atomistic calculations (by Normand Modine at Sandia Laboratory) in order to simulate the large-scale response of the electrons to strain. In addition, employ the Luttinger Hamiltonian for the

valence band structure to determine the structure of the light and heavy holes and in particular their mixing effect in the presence of sample edges (i.e., the wire perimeter) and strain due to lattice mismatch.

Approach

The basic tool for calculating the electronic structure in nanowires is a self-consistent electronic structure code, which I wrote, called SETE. This code uses a Newton-Raphson algorithm to solve the Poisson and Schrödinger equations self-consistently while using a local density approximation to include the effects of exchange and correlation. The method is also applied to the electronic structure of quantum dots and molecules in the vicinity of metallic surfaces. In addition, for the case of strain in nanowires, SETE will be modified to include both the deformation potential due to lattice mismatch effects as well as the Luttinger Hamiltonian to handle the complex valence band structure.

Accomplishments

The SETE calculation for InAs nanowires in the presence of scanning probe tips is working and we are now calculating various configurations (for double dots, for example) to study the influence of tip on conductance characteristics. The theoretical analysis of the Luttinger Hamiltonian is complete and the SETE code for the Laplacian is

being modified for the case of the valence band in a complex geometry. We do not yet have any results on strain fields.

Surface Enhanced Raman Spectroscopy

Goals

In conjunction with the Defense Advanced Research Projects Agency (DARPA), the theory group of <u>Alan Aspuru-Guzik</u> (Chemistry) and the experimental groups of <u>Ken Crozier</u> (SEAS) and <u>Eric Mazur</u> (SEAS), I am working to calculate the enhancement to Raman spectroscopy that arises from the exchange of electrons between a molecule and an adjacent metal nanoparticle or nano-structured surface.

Approach

Raman spectroscopy involves the absorption of light be a molecule and the virtual excitation to an excited electronic state, followed by the decay of the molecule to the ground electronic state, but in an excited vibrational state. The emitted photon in this second process is therefore of longer wavelength than that of the incident photon and the shift is therefore proportional to the vibrational excitation energy. Analysis of this process requires, in general, a treatment of the time-dependent evolution of the molecule in the presence of the external electric field. For surface-enhanced Raman spectroscopy, the properties of the surface, including its plasmon spectrum, must be included in the analysis. One of our main approaches is to employ the mature *ab initio* electronic structure code "octopus" for computing the electronic structure, but to further embed that code in the SETE code in order that the interaction with the surrounding metal material may be properly included.

Results

The octopus code has been properly interfaced with the SETE code and a tests case,

the hydrogen molecule between parallel metallic plates, has been successfully computed. Further, more realistic tests are currently underway.



Goals

Recent experiments have shown that semiconductor nanoparticles (CdSe) can capture photons more efficiently that ordinary photovoltaic materials and, when spread on the surface of photovoltaic materials can significantly increase the efficiency. This work seeks to compute the exciton transfer process in realistic systems by calculating the interacting state of the nanoparticles and also the matrix elements for transfer events in a background of metallic leads.

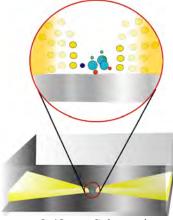


Figure 8.48. Schematic of molecule between nanofabricated antennas employed for surface enhanced Raman spectroscopy.

Approach

The Förster matrix element involves an integral over the product of the envelope portion and Bloch portion of the wave function. This integral can be split into parts, which involve (i) the material properties and (ii) the large-scale structure of the exciton. Further, in contrast to previous work, we have developed a method for expanding the interaction about the unit cell, as opposed to the nanoparticle center, which makes the calculation significantly more accurate for particles that are closer to each other than either of their radii. Finally, the use of Poisson's equation to determine the matrix elements allows the computation of the transfer rate without requiring, at any stage of the calculation, the explicit calculation of the kernel of the Coulomb interaction in the complex environment.

Results

The electronic structure calculation has been completed and results for the efficiency of energy transfer are currently being written-up. A presentation of the work at the 2009 APS March Meeting will be given.

Tuning a Double Quantum Dot in an InAs/InP Nanowire with an SPM Tip

Robert M. Westervelt

SEAS and Physics, Harvard University

Collaborators: Donhee Ham (SEAS, Harvard), Eric Heller (Chemistry and Physics, Harvard)

International Collaborators: Daniel Loss (University of Basel), Lars Samuelson (Lund University), and Seigo Tarucha (University of Tokyo)

Research Goal, Approach and Accomplishments

The goal of this research is to develop ways to individually tune the charge of tunnel coupled nanowire double dots, by using the conducting tip of a cooled scanning probe microscope (SPM) as a movable gate. Using chemical beam epitaxy, Samuelson's group can grow very small InAs quantum dots defined by InP barriers. The dots are shaped like hockey pucks, and tunneling occurs along the flat faces. These quantum dots have the advantages that they can be very small (~20–50 nm diameter by ~20 nm thickness), increasing the energy spacing of electron quantum states, thereby permitting operation at higher temperatures, and that the g-factor for electrons is large, easing the manipulation of spins for spintronic applications. However these dots can be difficult to control using conventional lithographically fabricated side gates, because their size is comparable or smaller than the spatial resolution of e-beam lithography.

We will tune the charge on nanowire double dots by using the tip of a cooled SPM as a movable gate, as illustrated by the simulations in Figure 8.49. A device is made by attaching source and drain leads to a nanowire that lies sideways on a substrate; the SPM tip is scanned in a plane slightly above. The number of electrons on a dot is controlled by the charge $C_{td}V_{tip}$ induced by the tip where the tip-to-dot capacitance C_{td} and V_{tip} is the tip voltage. By varying the tip-to-dot distance, the numbers of electrons m and n on the two dots can be individually controlled, as shown in Figure 8.49.

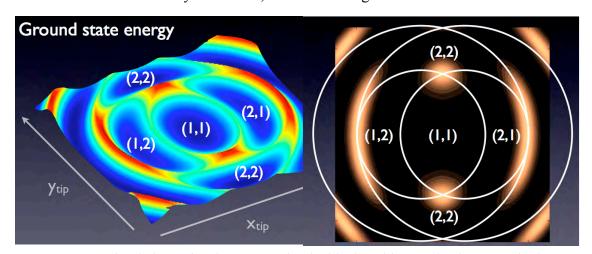


Figure 8.49. Simulations of tuning a nanowire double dot with a conducting SPM tip that acts as a movable gate: (*left*) Ground state energy of the double dot *vs.* tip position with fixed tip voltage – the number of electrons on the left and right dots are indicated, (*right*) Double dot conductance *vs.* tip position showing Coulomb blockade peaks.

Experiments will measure the conductance image for the double dot, shown on the right in Figure 8.49. For the series double dot, conductance can only occur when both dots are on a Coulomb blockade conductance peak, at the boundary between m and m+1 electrons in the charging diagram, shown at left. So the simulated conductance image of double dot vs. tip position, shown on the right, has peaks where the bulls eye patterns for the two dots overlap. In the experiments, this pattern of peaks will define the charging diagram.

These simulations show that an SPM tip can be used to individually control the charge on each dot in a double dot structure via its position. This approach will allow us to conduct a full range of experiments to manipulate the charge and spin on double dots grown inside heterostructure nanowires.

In addition to the nanowire dot experiments, <u>Westervelt's</u> group is assembling two custom-made cooled scanning probe microscopes for use in this work. The SPM imaging heads are fabricated in Harvard's machine shop, and the custom control electronics is designed and built in our electronics shop. The SPM control software was written by a previous graduate student, Mark Topinka.

Scanning SET Imaging of Graphene

Amir Yacoby

Physics, Harvard University

Collaborators: Carol Lynn Alpert (Museum of Science, Boston); Gloria Hoefler

(Agilent Technologies); (Zhifen Ren (Boston College)

Research Goal, Approach and Accomplishments

The quantum Hall effect is manifested in transport through vanishing longitudinal resistance and a quantized transverse resistance. In graphene, the relativistic nature of the underlying particles and the absence of valley mixing give rise to quantum Hall phases at filling factors y = 4i - 2 where the 4-old degeneracy is a result of both spin and valley degeneracies. To date it is well established that disorder plays a crucial role in the formation and robustness of quantum Hall phenomena. While at low magnetic fields the relativistic nature of the electronic spectrum of graphene prevents particle localization, the application of a strong magnetic field perpendicular to the layer opens up Landau gaps in the spectrum that lead to strong localization. Clearly the universal nature of the quantum Hall effect in macroscopic specimens relies on its insensitivity to the details of the underlying disorder mechanism. Already single particle physics of two-dimensional electrons in a disordered potential landscape leads to localization of charge and scaling behavior. However, in high mobility GaAs specimens localization is no longer solely driven by disorder and a fundamentally different picture of localization emerges that is strongly influenced by the presence of Coulomb interactions leading to Coulomb blockade and nonlinear screening of the disorder potential.

Thus far Coulomb interactions in clean two-dimensional electron systems are known to have a profound effect and may bring about for example the fractional quantum Hall effect and quantum Hall ferromagnetism. The latter was recently observed in graphene. However, the carrier mobility in nonsuspended graphene, a common measure of the disorder strength, is typically 10^3 to 10^4 times smaller than the mobility characterizing GaAs based 2-D systems. Even in suspended layers peak mobilities are up to a hundred times smaller than those measured in high mobility GaAs layers. It raises the question whether Coulomb interactions play a significant role in particle localization in graphene or perhaps single particle physics suffices. To address this issue, we explore the electronic density of states in graphene at high magnetic field using a scanning single electron transistor. We focus our work on the quantum Hall regime where we image the bands of localized states both in position and energy. Our findings clearly indicate that at large magnetic fields charge localization is governed by the presence of strong Coulomb repulsion between electrons despite the high level of disorder and the behavior is similar to the one observed in GaAs two-dimensional electron systems with their much larger carrier mobilities.

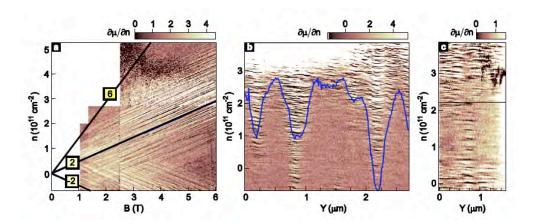


Figure 8.50. Measured spectrum of localized states in graphene. **a.** Color rendition of the inverse compressibility measured as a function of average carrier density (controlled using the back gate) and external magnetic field. The measurement is taken at a single location above the flake. Localized states in this measurement appear as dark lines that run parallel to the filling factor. **b.** Color rendition of the inverse compressibility measured along a line across the graphene flake and as a function of average carrier density. Localized states in this measurement appear as dark horizontal lines spanning a small spatial extent determined by the localization length or by the resolution limit of the tip. The solid line indicates the carrier density profile along the same line extracted from the surface potential measurements. **c.** Localized state spectrum of a single dot. The level spacing is inversely proportional to the size of the dot and yields a measured dot size of 60 nm.

SEED: Single-Photon Photonic Device

Marko Lončar

Physics, Harvard University

Collaborators: Vladimir Bulovic (Massachusetts Institute of Technology); Phil

Hemmer (Texas A&M); Misha Lukin (Harvard University)

Number of postdoctoral fellows: 0 Number of graduate students: 1 Number of undergraduate students: 0

The work sumamrized here, resulted in three journal publication¹⁻³, two conference papers^{4, 5}, and four conference talks given by PI's students and postdocs. The work was also featured in three invited conference talks that PI gave. Finally, one manuscript has been submitted for publication⁶, and three manuscripts are in preparation.

Research Goal, Approach and Accomplishments

In this funding period we focused on four projects related to diamond photonics, and in particular application of color centers in diamond for quantum information processing. Nitrogen-vacancy (NV) color centers embedded in diamond have emerged as promising platforms for single photon sources, and quantum systems in general. NVs form a basis for a very promising approach to a few-photon all-optical switches, since they combine the key advantages of isolated atomic systems with solid-state integration, and have following unique optical properties: (i) room temperature operation, (ii) little inhomogeneous broadening, (iii) deterministic positioning using ion implantation. In order to further improve the efficiency of NV-based quantum-emitters, it is important to enhance the photon production rate as well as the collection efficiency of emitted photons. This can be achieved by embedding NCs within optical structures including cavities, waveguides and nanowires. A major challenge, however, is the fact that the zero phonon line (ZPL) optical transition is in the visible (637 nm), and structures must therefore be designed in a visibly transparent material. One option is diamond, which has a reasonably high refractive index n = 2.43, but experimentally this can be very challenging. Alternative approach is based on diamond nanocrystals embedded within wide band-gap materials such as silicon nitride (SiN_x), titania (TiO₂), hafnia, etc.

a) Single-photon Devices Based on Diamond Nanocrystals Embedded in SiN_x and TiO_2 Platforms

Due to their "nanoparticle" nature DNCs can easily be integrated/embedded within passive nanophotonics platforms that we have recently developed in following material systems (suitable for operation in visible): silicon-nitride (Si_3N_4), titanium-oxide (TiO_2), and gallium-phospide (GaP). DNCs positioned in the proximity of high-Q cavity will be strongly coupled to the cavity field, and therefore allow broad-band switching function based on the methods discussed above. By interfacing optical cavities with low-loss waveguides (losses ~ 1 dB/cm), and using efficient spot-size converter couplers (coupling efficiency > 90%), we can control interface our devices with external optical systems.

Moderately low refractive index of materials that are transparent invisible has often been considered an impediment to ultra-high-Q photonic crystal nanocavity designs, which thus far have only been demonstrated in high-index semiconductors such as silicon. Last year, however, we designed for the first time a SiN_x photonic crystal nanocavity with a Q factor of 1.4 ×10⁶ and a mode volume of \Box 0.78(λ /n)³, which represents a breakthrough in the design of photonic crystal devices¹. We have also

modelled the effect of a diamond nanocrystal (DNC) (~40 nm particle) positioned on top of the cavity or embedded in the middle of the cavity, and we found that Qs greater than 10^6 are still possible. Moreover, we predicted that NV center embedded in such DNC would experience reduction of radiative life time from ~15 ns to ~2 ps due to the Purcell factor of about 7,000. This is a significant improvement for an NV-based single photon source. Moreover, we predicted that our DNC-nanocavity system can enter so-called "strong coupling regime" of light matter interaction, in which the coherent dynamics between the emitter and the cavity mode dominate the dissipative loss rates from the system. With an NV center positioned on the top surface of the cavity, we found the relevant rates for strong coupling dynamics to be $(g, \kappa, \gamma) = (0.52, 0.23, 0.05)$ GHz, where g is the Rabi frequency, κ is the cavity loss rate of the highest Q cavity, and γ is the spontaneous emission rate of the NV center. As such, our system is a promising platform for integrated quantum optics with diamond NV centers.

Our devices have been made in CNS at Harvard using stochiometric Si₃N₄ on Si substrate (Figure 8.53b). The fabrication sequence⁵ consists of electron beam lithography, reactive ion etching and sacrificial removal of Si substrate to realize free-standing nanobeams with photonic crystal cavities defined within. A custom-built confocal microscopy setup was used for the initial characterization of the 1-D cavities. Typical fluorescence spectrum of the tested devices⁵ with slightly elliptical air holes is shown in

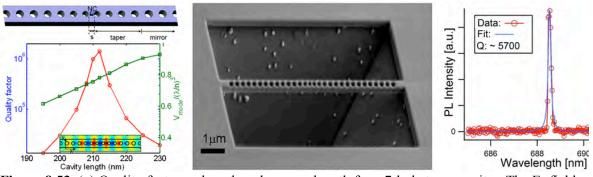


Figure 8.53. (a) Quality factor and mode volume vs. length for a 7-hole taper cavity. The E_y field for the cavity mode is shown in the inset. (b) Si_3N_4 air bridge PC nanocavity. (c) PL spectra of cavity emission.

Figure 8.53c. The linewidth of the resonance is 0.12 nm, which corresponds to a Q factor of approximately 5,700, and is limited by the resolution of our spectrometer. The planar nature of the fabricated structure allows integration of a large number of optical cavities with nanocrystals embedded within them on the same chip. By interfacing optical cavities with low-loss waveguides (Figure 8.54) we can efficiently couple photons in and out of the cavity and wire-up multiple cavity/quantum emitter nodes, entangle different qubits, or efficiently extract light from such a quantum chip using fiber couplers. The same cavities are being used to enhance optical properties of colloidal quantum dots synthesized by Moungi Bawendi (MIT). It is also interesting to notice that our optical resonators are free to move, though we have not taken into account mechanical degrees of freedom yet. We are currently pursuing several research directions that will combine fields of nanophotonics and NEMS, exploit optical and mechanical degrees of freedom of free-standing nanobeams, and result in novel reconfigurable optical and quantum-optical devices.

Alternative platform that we studied in this period⁶ is based on a quantum emitter placed in the strong optical field that exists between two waveguides in close proximity (Figure 8.54b). The large cooperativity ($C = g^2/\kappa\gamma >> 1$) of such system, and strong coupling between an emitter and a photon can be used to realize efficient single-photon

sources, photon registers, and single-photon switches. We have recently predicted

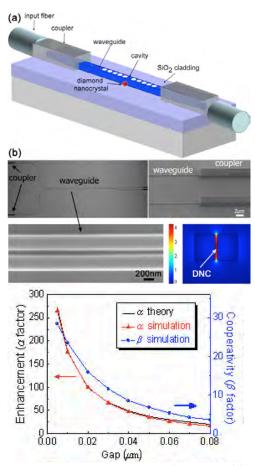


Figure 8.54. a) Integrated, waveguide coupled, single-photon device based on strongly coupled NV center. b) Fabricated waveguides and couplers. Blow-up of the slot-waveguide section is shown. Inset shows optical energy stored in the slot. NV placed in the high-optical field would experience large cooperativity and would interact strongly with waveguide mode.

theoretically⁶ that this so-called "slotwaveguide" configuration can enable cooperativity larger than 20 (comparable to cavity-OD case discussed above) over 100 nm wide bandwidth, much wider than what can be achieved with a high-Q cavity. This is also very attractive for exploration of fundamental properties of quantum emitters. For example, in collaboration with Bawendi group we are developing waveguide platform that would allow them to perform spectroscopy on individual colloidal quantum dots placed in the slot-waveguides.

b) Single-crystal Diamond Nanowires for Efficient Light-matter Coupling

In 2007 we demonstrated, for the first time, that diamond nanowires fabricated topdown using focused-ion beam milling can be used to isolate and study individual NV color centers in diamond⁴. That work was also featured as one of the highlights of our NSEC center. In 2008 we significantly expended our research efforts on diamond nanowires. First, using numerical modeling, we demonstrated that these devices can be used for efficient extraction of photons generated from NV centers. We examined optimal nanowire shape that mazimizes coupling between NV center and guided optical mode of the nanowires, and minimizes the reflection of light from the top nanowire facet. Both of these effect significantly improve the collection efficiency of photons emitted from NV. Next, we developed fabrication procedure based on

reactive ion etching that enables us to realize large number of nanowires. First, various types of randomly positioned nanoparticles (Au, Ag, AlOx, SiO2, polysterine), deposited via drop-casting, have been used as mask to etch single-crystal diamond (Figure 8.55a). Once etch recipe was optimized, e-beam lithography follwed by reactive ion etching was used to realize large number of ordered single-crystal nanowire arrays (Figure 8.55b). In this way we could control the size of our nanowires (a.k.a. nanocones) which in turns determines the optical properties of nanowires.

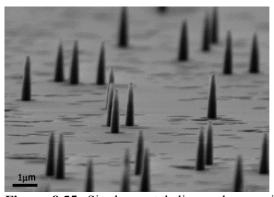




Figure 8.55. Single-crystal diamond nanowires fabricated using top-down fabrication based on reactive io5 etching. **a**) Au nanoparticles deposited via drop-casting have been used as etch mask. **b**) e-beam lithography has been used to realize ordered arrays of diamond nanowires

Home-built scanning confocal microscope was used to characterize our diamond nanowires. In Figure 8.56 we show the confocal photoluminescence image of an array of

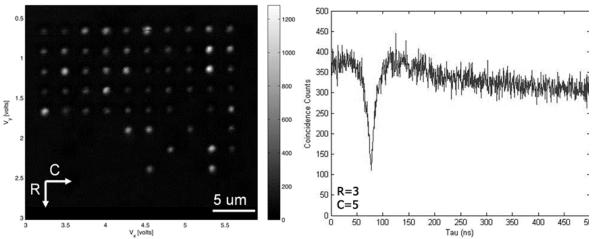


Figure 3.56. a) Confocal microphotoluminescence image (excitation: CW 532 nm; collection time: 5 ms, wavelength of collected signal: 637 nm–700 nm) of an array of diamond nanowires. **b**) g₂ second-order correlation function of photons emitted from a nanowire in the third row and fifth column. The dip is the signature of anti-bunching which is the indication of single-photon emission.

nanowires pumped with green light (1 mW power). The image is formed by collecting the red light emitted from NV centers. Our approach allows us to collect close to an order of magnitude more phtons from our nanowires than from diamond nanocrystals. This is a very important result and clearly illustrates the advantage of nanowires for efficient photon extraction. Next, we measured second-order correlation function (g₂) for photons collected from nanowires (Figure 8.56b) and we observed the dip in g₂ for large number of devices. Such dip is characteristic of so-called anti-bunching which is the signature of single photon emission. Therefore, based on our measurement we conclude that our diamond nanowires have individual NV color centers embedded in them. This is an excellent result and, to the best of our knowledge, the first demonstration of single-photon emission in any micro-fabricated structure ever made in single-crystal diamond. Our nanowire work and the diamond nanophotonic technology that we are developing will play an important role as an enabling technology for fundamental quantum optics experiment, quantum information processing based on diamond, as well as bio-sensing applications based on magnetometry. We are currently preparing a

manuscript based on these results, that will be submitted to high-impact journal. Number of groups at Harvard and around the world have expressed interest in our techniques and results. Moreover, we had several contacts with companies (Advanced Diamond Technologies, Apollo Diamond) that have expressed interest in our technology, but it is still too early to make predictions on potential comemrcial impact.

c) Other Work supported in Part by NSEC

With support from NSEC, we completed several additional projects and looked at various properties of quantum emitters placed in strong optical fields.

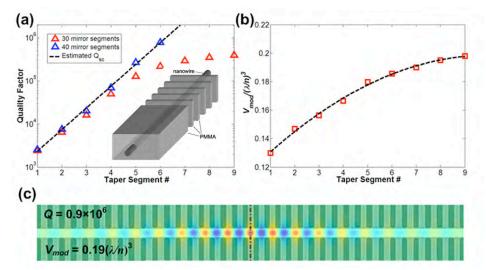


Figure 8.57. High-Q optical cavity based on a semiconductor nanowire embedded in PMMA grating.

In the first publication², we proposed a platform to achieve ultra-high Quality factor (Q) optical resonators based on semiconductor nanowires. By defining one-dimensional photonic crystal at nanowire ends and engineering the microcavity pattern, cavities with Q of 3×10^5 and mode volume smaller than $0.2(\lambda/n)^3$ have been designed. This represents an increase of almost three orders of magnitude over the Quality factor of an as-grown nanowire. Our cavities are well-suited for the realization of nanowire-based low-threshold lasers, single-photon sources and quantum optical devices that operate in the strong-coupling limit. Our system is similar to micropost (micropillar) optical resonators that have been used in vertical cavity surface-emitting lasers and single-photon sources. However, our approach requires simple fabrication procedure that combines bottom-up nanowire synthesis with top-down single-step e-beam lithography.

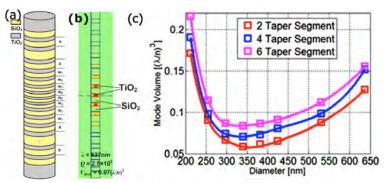


Figure 8.58. High-Q optical cavity based on a semiconductor nanowire embedded in PMMA grating.

Next, we looked at similar system, based on nanoscale micropost pillars³ and we have demonstrated that high Quality factor micro-pillar cavities can be realized with sub-micron diameter pillars. We propose novel micropost /micropillar cavity designs with high

Quality factor ($Q \sim 3 \times 10^6$) and record low-mode volumes [$V \sim 0.1(\Box/n)^3$] based on the TiO₂/SiO₂ material system. The proposed cavities have Q/V three orders of magnitude larger than previously reported ones. We showed that our cavity embedded with diamond nanocrystal provides a feasible platform for cavity quantum electrodynamics experiments in the strong coupling limit. The proposed structure can be easily adapted to different material systems and enable realization of an ultra-high Q/V cavity in AlAs/GaAs platform suitable for realization of low-threshold VCSELs, for example.

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9. CENTER DIVERSITY—PROGRESS AND PLANS

The NSEC based at Harvard University is committed to increasing the diversity of the science and engineering workforce, and to making science and engineering accessible to a broad audience. NSEC faculty participants are dedicated to increasing participation by members of underrepresented groups and to giving these scientists and engineers the resources and guidance needed to succeed in each stage of their careers so as to become leaders in both education and research. Our strategic plan for increasing diversity builds on connections we have made through various programs, and seeks to increase our impact by developing new partnerships, both internally and externally. The recently released reports of the Task Force on Women Faculty and the Task Force on Women in Science at Harvard present several opportunities for leveraging NSF and University support to increase participation of women and underrepresented groups in science and engineering.

We have identified five broad goals that will be accomplished through a variety of initiatives: (1) To intensify the recruiting, support and professional development of a more diverse group of graduate students and postdoctoral researchers; (2) to increase the diversity of faculty participating in the NSEC; (3) to strengthen recruiting and mentoring of members of underrepresented groups through our joint REU programs; (4) to mentor pre-college students as they consider careers in science and engineering; and (5) to develop long-term partnerships with predominantly female and minority-serving institutions.

Goal 1: Recruiting, Professional Development and Support of a Diverse Group of Graduate Students and Postdoctoral Researchers

Graduate students and postdoctoral researchers are at crucial stages in their careers. Their experiences in terms of professional development, mentoring, and access to facilities and other opportunities have a significant impact on their career choices. Our goal is to leverage NSF and University support to recruit graduate students and postdoctoral researchers from underrepresented groups in science and engineering, and to provide resources to the students that will empower them to become educational and research leaders.

Strategy 1: Recruiting. Many of the strategies in place in the REU program to recruit highly qualified undergraduates to the summer program have been shared in recruiting of graduate students and postdoctoral researchers, including publicizing the graduate program and postdoctoral positions at conferences and on websites that reach a large population of underrepresented minorities. The Director of Educational Programs Kathryn Hollar coordinates with the Minority Recruitment Officer for the Harvard Graduate School of Arts and Sciences and the Graduate Program Administrator in Physics to share resources in these efforts.

More directly, we are using the REU program as a method to recruit students to our graduate programs and encourage students to continue on to graduate school in general.

Since 2002, at least 20 former REU students have been accepted into graduate programs at Harvard, including minority students and 12 women. Twelve of these students are currently graduate students at Harvard (3 minority and 6 women).

Strategy 2: Professional Development and Mentoring. The NSEC has developed a program of professional development for NSEC-affiliated graduate students and postdoctoral researchers through the research exchange seminar and the AP298r course. Postdoctoral researchers and graduate students also have the opportunity to participate in our educational programs, including developing mentoring and project management skills through our REU program and experience in presenting to K-12 classrooms through connections with the Cambridge Public Schools and our RET programs, and engaging the public at the Museum of Science, Boston.

The NSEC will also work in concert with the School of Engineering and Applied Sciences, the Chemistry and Chemical Biology Department, and the Physics Department and the University administration to leverage support for more professional development opportunities for graduate students and postdoctoral researchers. We will use some of our funding to support these professional development activities and for travel support.

Strategy 3: Support. We have established Center fellowships to encourage the participation of women and minority groups in science and engineering. Fellows are integrated into the research and educational community of the NSEC, and connections with faculty and institutes across the university are facilitated through this program. Access to research facilities and educational and professional development opportunities helps develop a strong pool of well-prepared researchers for faculty positions and the scientific community. In 2008–2009, these Postdoctoral Fellows include:

Dr Lyuba Kuznetsova (Advisor: Capasso)

• Dr. Maria Fyta (Advisor: Kaxiras)

• Dr. Crystal Ripplinger (Advisor: <u>Parker</u>)

• Dr. Malancha Gupta (Advisor: Whitesides)

Strategy 4: Diversity Working Group. For the past 2 years, we have invited graduate

students, postdoctoral fellows, and undergraduates to attend the joint annual meeting of the National Society of Black Physicists and **National** Society of Hispanic Physicists. Out of these meetings, a core group of minority graduate students and postdoctoral fellows have started meeting regularly to discuss strategies for recruitment, retention and



Figure 9.1. Diversity working group meets with chair of physics Christopher Stubbs and graduate programs administrator Sheila Ferguson to discuss initiatives for increasing diversity in the physical sciences at Harvard.

professional development of minority scientists and engineers (Figure 9.1). One initiative that this group has undertaken is to informally mentor minority students in our REU program. We will continue to meet with these students and postdoctoral fellows to follow up on several suggested initiatives, including increased participation by Harvard undergraduates in national conferences, working with our undergraduate and graduate admissions office to recruit talented minority students to Harvard, developing a speakers bureau of faculty and postdoctoral fellows who are interesting in recruiting at HBCUs and MSIs, and developing metrics for tracking achievement and movement of minority students through Harvard.

Goal 2: Increase Diversity of *Faculty* Participating in NSEC

One of the major challenges facing the science and engineering community is to increase the diversity of the faculty ranks. The collaborative and interdisciplinary nature of the research of the NSEC provides a supportive environment that effectively integrates young scientists and engineers into a vibrant scientific community at the beginning of their academic careers. The NSEC also provides access to cutting-edge instrumentation facilities, which are a valuable resource at an early career stage.

Strategy 1: Partnership with Radcliffe Institute. As discussed in Section 12, we partnered with the Radcliffe Institute this past year. Radcliffe Fellows continue to collaborate with NSEC faculty; recent examples include Dr. Tayhas Palmore, 2006–2007 Radcliffe Fellow and Paula T. Hammond, 2003–2004 Radcliffe Fellow.

Strategy 2: Leadership and Focus in Faculty Hiring. The sciences and engineering at Harvard are experiencing a period of rapid growth, and faculty in the NSEC are in leadership roles at Harvard that can influence the recruitment and support of new faculty. The highly collaborative environment of the NSEC and the availability of world-class instrumentation also provides an ideal opportunity to develop the careers of new faculty. Junior faculty at Harvard contribute significantly to each research cluster within the NSEC. Close interaction with senior faculty helps new faculty to develop stronger individual research and educational programs. Senior faculty in the NSEC who are also in leadership positions at the department and university level include:

Professor **Cynthia Friend**: Former Chair of Chemistry and Chemical Biology Professor **Robert Westervelt**: Member of Diversity Committee, Physics Department Professor **Howard Stone**: Associate Dean of Academic Programs, SEAS

Professor Venkatesh Narayanamurti: Former Dean of SEAS

Since 2002, we have increased the number of junior faculty supported by the NSEC from 1 in 2002 to 7 in 2008; the number of women faculty supported has increased from 1 in 2002 to 5 in 2008. In 2007, <u>Joanna Aizenberg</u> was hired as a senior faculty in SEAS and CCB, and has assumed leadership roles as a member of the Executive Committee for the NSEC, and as part of the Directors Group for CNS.

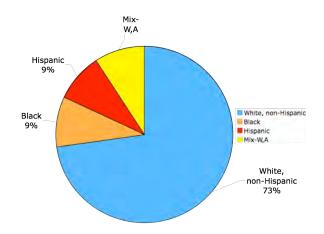
Goal 3: Strengthen Recruiting and Mentoring of Underrepresented Groups through REU Program

NSF support for the REU programs of the NSEC and allied programs in Materials Research provides core funding for a growing undergraduate research program that includes substantial funding from Harvard. These joint programs, which now support over 45 students each summer, share a common infrastructure for recruiting, providing community and professional development activities during the program, intensive mentoring during the summer and post-program, and program evaluation and tracking. Connections made through our REU program's focus on diversity also serve as critical building blocks for our strategic diversity plan.

Strategy 1: Recruiting. A special initiative spearheaded by Howard Stone recruits and engages excellent students from Historically Black Colleges and Universities (HBCU) in our summer REU programs. This recruiting effort has expanded to include universities with predominantly Hispanic enrollments, and primarily undergraduate institutions that serve women. Faculty and staff have visited Morgan State University, Howard University, Morehouse College, Spelman College, Florida Agricultural and Mechanical University, the University of Puerto Rico (Rio Piedras and Mayagüez campuses), Sweetbriar College, Texas Prairie View Agricultural and Mechanical University, and North Carolina Agricultural and Technical State University. At these recruiting visits, we discuss not only the opportunities available at Harvard, but also the characteristics of a strong application for a research experience program. Former REU students at these institutions often lead discussions on the summer research experience. Additionally, faculty and staff recruit at professional and research conferences and career fairs for underrepresented groups, including the joint annual conference of the National Society of Black Physicists and the National Society of Hispanic Physicists; the National Society of Black Engineers, a National Conference on Hispanics in Engineering; New England Board of Higher Education Minority Career Fair at MIT. To reach a wider audience of

applicants for our REU program, we partner with the Graduate Admissions Offices of various departments, including SEAS and Physics, to distribute materials advertising our program at these conferences and career Attendance at these conferences aids us in recruiting students and in following up with past REU alumni. In 2008, we recruited 5 very talented students from these conferences to our REU program.

In addition to these recruiting visits, we also advertise on many websites and listservs that are resources for



Figgure 9.2. Racial and ethnic demographics of students receiving NSF support through NSEC.

underrepresented groups. REU participants report that the internet is an important resource for finding summer programs; therefore, we also advertise on web sites and listservs that target underrepresented groups in engineering). These efforts resulted in an increase in applicants to the joint programs from 247 in 2004 to over 500 in 2008. Applications for the 2009 REU program are projected to be in excess of 600. Figure 9.2 shows the demographic make-up of the 11 REU participants who were fully or partially funded through the NSEC. Of these students, 2 were from underrepresented racial or ethnic groups in science and engineering, and 3 were female. Of the 11 participants, 5 were sophomores, 5 were juniors, and 1 was a senior. Two students were from primarily undergraduate institutions; 7 were non-Harvard students. Over half of the students had no prior research experience.

Strategy 2: Mentoring and Professional Development. The summer REU program includes many community-building and professional development activities for both REU participants and mentors, including a workshop on presentation skills, a luncheon on applying to graduate school, and weekly presentations by faculty on research and ethics.

Strategy 3: Post-Program Mentoring and Long-term Tracking. The relationships developed during the program extend past the summer: Mentors provide guidance and support as students apply to graduate school, and also include students in the process of writing and submitting papers that are based on their summer work. Students are encouraged to present their work at local and national conferences, and funds are available through the REU/RET Site in Materials Research to support travel for mentors and REU participants to national conferences.

Goal 4: Introduce *Pre-college Students* to Science & Engineering Programs through Summer Opportunities or Year-Round Programs

We continue to expand our repertoire of activities for pre-college students and teachers, focusing on collaborations that effectively impact schools and students that have high need or significant achievement gaps between student groups. We continue an informal partnership with the Cambridge Public Schools, and are developing a collaboration with a relatively new public school in Boston, The Engineering School at the Hyde Park Educational Program. Both of these schools have significant populations of students who have historically been underrepresented in science and engineering careers. The Cambridge Public School District is an urban district that is over 60% minority, with 37% of students enrolled in a free or reduced lunch program. The Engineering School, one of the small schools that are a result of the recent reorganization of several large Boston Public Schools into smaller learning communities, is comprised of 56% Black and 34% Hispanic students, with 65% of the students enrolled in a free or reduced lunch program. In both partnerships, we focus on supporting students in school-based scientific research or engineering design projects, rather than formal curriculum development. This strategy capitalizes on our strengths as a highly disciplinary research institution, and allows us to meet critical student and teacher needs in terms of mentorship and professional development skills that are not explicitly covered in science curricula.

Strategy 1: Increase Collaboration with Cambridge and Boston Public Schools at the High School Level.

A new partnership with The Engineering School (TES) at the Hyde Park Educational Complex builds on the model developed with Cambridge Public Schools. The NSEC has supported the goal that TES has to increase student engagement in science and engineering competitions by providing expertise and feedback on student-defined science and engineering fair projects via email, class and student visits to Harvard, and visits to TES. Following the model developed with CRLS, our graduate students and postdoctoral fellows have worked with TES students on poster presentation skills, experimental design, and finding resources for projects (Figure 9.3). As discussed in **Section 11—Education**, we were also successful in securing a grant from the Boston Public Schools to continue this science fair support, and add research internship opportunities for TES students.



Figure 9.3. *Left*, 9th grade students from The Engineering School meet with Harvard undergraduates to discuss ideas for science and engineering expo projects. *Right*, TES seniors work with graduate student Andres Martinez (Whitesides research group) on a science fair project on paper diagnostics.

Strategy 2: Continue Collaborations with Cambridge Middle Schools, Parents, and the Community. As discussed below in *Section 11—Education*, NSEC faculty participate in Project TEACH (The Educational Activities of Cambridge-Harvard), which brings each 7th grade class from CPSD to Harvard for a college awareness and science presentation day.

Strategy 3: Develop Connections with Urban Schools through RET. Our RET program recruits teachers from local urban schools to participate in the Center's research and educational activities for 6–8 weeks during the summer. We encourage many follow-up activities with teachers, including classroom visits and field trips to Harvard. As we continue to build research and educational programs in close partnership with CPSD and Boston Public Schools, we will integrate our RET teachers and their students into these activities. For example, a middle school teacher from CPSD participated in our joint RET programs in Summer 2008, and we had 2 teachers from The Engineering School who were a part of our RET program in 2008 (see discussion in *Section 11—Education*).

Strategy 4: Pursue Internal Partnerships. A partnership with the Harvard Graduate School of Education has developed links with pre-service teachers in the sciences through the NSF Noyce Scholarship Program. In the first year of the 3-year Noyce program, several teachers took graduate science or engineering courses with NSEC faculty. In the second year of the grant, a Noyce Scholar was recruited to our RET program.

These four initiatives, natural extensions of established relationships, are examples of how we will continue to develop science education partnerships that engage students, teachers, and parents.

Goal 5: Develop Long-term Research and Eeducational Collaborations with Predominantly Female or Minority-Serving Institutions

In March 2007, we also hosted a visit by students from Morehouse College as part of their annual graduate program trip during spring break. In fall 2007, <u>Eric Mazur</u> visited Morehouse College and publicized the REU program during his visit. As a result, we recruited 2 students from Morehouse College to participate in our REU 2008 program.

Our goal over the course of NSF support is to formalize these research and educational partnerships with predominantly female and minority-serving institutions by facilitating the exchange of educational strategies and developing research collaborations.

10. Education and Human Resources

Center participants continue to be actively involved in programs that engage the public, teachers, students, and young scientists and engineers in the excitement of scientific discovery and increase awareness of the impact of scientific research on their daily lives. Our broad goals are to increase public engagement in and awareness of advances in nanoscale science and engineering, and to promote career advancement for a diverse group of young scientists who represent the future of science and engineering. Our educational initiatives at the pre-college, undergraduate, graduate, and postdoctoral levels include embedded diversity initiatives and strategic collaborations whenever possible to encourage individuals from underrepresented groups to pursue careers in science and engineering. In addition to increasing public understanding of nanoscale science and engineering, our long-standing partnership with the Museum of Science, Boston enhances the university-based activities such as our REU and RET programs, as well as professional development of postdoctoral fellows and graduate students.

10.1 Public Engagement

10.1.1 Holiday Science Lecture for Children and Families

Current Activities. For the seventh year, Professor Howard Stone, along with HSEAS Postdoctoral Fellow Amy Rowat, Daniel Rosenberg (Harvard Science Center

demonstration staff), and Educational Programs Director Kathryn Hollar developed and presented our annual interactive Holiday Lecture. This year's lecture, "From Bean to Bar: The Sweet Science of Chocolate," was held December 13, 2008 (Figure 10.1). This children- and family-friendly science presentation is modeled after the Christmas Lectures first presented by Michael Faraday at the Institution. Due to popular demand, this vear's lecture was presented twice to with over 500 people in attendance at each show.



Figure 10.1. <u>Howard Stone</u> enlists young audience members to help demonstrate different melting temperatures of fats present in chocolate.

Outcomes. The Holiday Lecture reaches now reaches over 1000 people each year, and is designed to encourage families to continue explorations and discussions of science post-lecture. Comment cards collected after each lecture indicate that Informal feedback via email from returning families each year indicates that the lecture has impacts beyond the 1-hour Saturday celebration of science.

Planned Activities. In spring 2009, we will give an encore performance of "The Sweet Science of Chocolate" during the Cambridge Science Festival to accommodate the waiting list of over 1000 people for the December performance. In May 2008, we will

also collaboratively perform the lecture at the University of New Mexico, co-presenting with faculty and graduate students in the NSF Partnership in Research and Education in Materials (partnership with the MRSEC, which co-sponsors the Lecture each year). We also plan to write and publish several articles that detail the design and delivery of the lectures since 2002, as well as some of the interactive demonstrations in the lectures.

10.1.2 Dragonfly TV

Current Activities. In spring 2008, the NSEC and MoS worked together to support filming of two *Dragonfly TV (DFTV) nano* segments on scale and carbon nanotubes. *Dragonfly TV* is a television show produced by Twin Cities Public Television that features middle-school students engaged in science inquiry or engineering design.

Outcomes. The DFTV episode with Harvard graduate students and staff will air this spring (2009) on local stations. Each DFTV episode is viewed by over 1 million people.

Planned Activities. We plan to disseminate complementary classroom activities developed by DFTV staff to local school partners at the elementary and middle school levels. Additionally, we are investigating the possibility of working with SciGirls, a also developed by producers of DFTV, to film additional episodes with research groups at Harvard.

10.2. Pre-College Activities

10.2.1 Project TEACH

Current Activities. Through a continuing program, NSEC researchers share their enthusiasm for science through Project TEACH (The Educational Activities of Cambridge and Harvard). This early college awareness program is a joint effort of the MRSEC, the NSEC-based at Harvard, and the Harvard Office of Community Affairs. Coordinated with the Cambridge Public Schools, Project TEACH brings each 7th grade class from the Cambridge Public School District to Harvard University throughout the school year. During the visit, students receive information about college admissions, and learn about college life from Harvard undergraduates. The class visit culminates in an interactive science presentation by a NSEC researcher on his or her research.

Outcomes. The program has reached over 300 students per year in past years; however, in 2007–2008, we have had fewer schools participate. Informal feedback from teachers indicates that increased pressure to prepare students for standardized tests, in conjunction with school cancellations due to weather, has reduced the number of field trips per year.

Future plans. Based on discussions with the Harvard Office of Community Affairs, and declining participation by schools, we plan to reconfigure the format of Project TEACH. One option is integrating this experience into a "Family Science & College Awareness Night" for each school so that parents or guardians can also be involved in discussions of college and science careers.

10.2.2 Research Experiences for Teachers (RET) Program

Current Activities. The NSEC, in conjunction with an REU/RET Site in Materials Research and Engineering and an RET Site of the National Nanotechnology Infrastructure Network, hosted 3 teachers in 2008. Teachers work with faculty, postdoctoral researchers, graduate students, and REU participants on research or science curriculum projects. Teachers commit to 6–8 weeks during the summer, and are invited for a second summer to refine educational modules that are developed.

In addition to a research/educational project, RET participants also attend weekly seminars on educational and research topics and on research ethics. The integrated nature of RET and REU activities, particularly the faculty seminars during the summer, provide opportunities for teachers to explore development of small classroom modules based on seminar content. RET participants also met weekly over lunch to discuss informally their research projects and how to best relate their summer research project to their curricula. The summer research experience for teachers culminates in a poster session. Teachers take these posters back to their classrooms to give students an introduction to scientific research, and to emphasize that science and engineering careers are accessible, interesting, and that science and engineering profoundly affect everyday life. These posters have also served as the basis for talks at regional and national conferences for teachers and faculty. Materials developed by teachers can be accessed at our website, www.eduprograms.deas.harvard.edu/RET.htm. NSEC-supported participant and project information can be found in Table 11.1.



Figure 10.2. *Left*, RET participants are trained on the SEM in the Center for Nanoscale Systems. *Center*, RET Joshua Bridger gives REU student Kenny Lyons, Jr. feedback on his NSF highlight. *Right*, RET participants talk with Prof. <u>Kit Parker</u> at the end of summer RET Poster Session.

Table 10.1: NSEC RET Participants, 2008

Table 10.1. INSEC RET Tarticipants, 2000	
RET Participant, Subject/School	Project Title(s)
Marc Abelard	Societal Implications of Paper Diagnostics;
Student support specialist/Partnerships	Science & Engineering Expo Curriculum
(The Engineering School, Hyde Park, MA)	
Joshua Bridger*	Electronics & Nanotechnology curriculum for
Physics (Dover Sherborn High School, MA)	high school AP courses
Rebekah Ravgiala	Paper Diagnostics for the Biology Classroom;
Biology (Tyngsborough High School, MA)	Measuring Inhibition of Microbe Growth by
	Colloidal Silver

Outcomes. This summer's work by NSEC RETs resulted in 2 classroom-tested modules and additional funding for student development for an urban public school. The Paper Diagnostics module was implemented in a biology classroom as a forensics "who-doneit" activity. Joshua Bridger built on prior summers to produce an extensive set of handson design modules on electronics for one semester his AP Physics course that include ties to current research at our NSEC. Based on his work in summer 2008, Marc Abelard worked to secure a grant for \$55,000 from Boston Public Schools for dual enrollment and research internships at Harvard for students at The Engineering School, a Boston Public School that has a minority majority population. Teachers also produced several videos of undergraduate and graduate researchers for use in their classrooms. We also scheduled follow-up field trips for 3 classes, and worked with individual students at The Engineering School on their science and engineering expo projects. The restructuring of our RET program to include more collaborative time between teachers also helped teachers in development of modules for their classrooms — more technologically savvy teachers helped teachers who were not as well-versed in tools such as powerpoint and word to develop their activities so that they were more interactive.

Planned Activities. RET participants will attend the National Science Teacher Association (NSTA) Annual Meeting in March 2009 to share modules with other RET participants across the nation through the NNIN RET program, and through the RET Networking meeting at NSTA. Several "mentor teachers" will return next summer to continue professional development, and help less seasoned teachers bridge the gap between the research environment and the classroom. Next summer, returning teachers will also focus on writing papers on tested modules for publication in peer-reviewed educational journals and for presentation at national conferences.

10.3 <u>Undergraduate Activities—REU Program</u>

Current Activities. The NSEC has increased the number of REU participants through substantial supplemental funding from the School of Engineering and Applied Sciences (SEAS), Harvard College, and the Rowland Institute at Harvard (<u>Frans Spaepen</u>, Director). An NSF-funded REU/RET Site in Materials Research (PI <u>Howard Stone</u>) has also allowed us to expand our professional development opportunities for participants. REU participants and projects are shown in Table 10.2.

Table 10.2: REU Participants, 2008

REU Participant/Institution	Project Title
Paul Aliotta/Eastern Nazarene College	Superconducting-insulator transition in aluminum nanowires
Monica Allen*/Harvard University	Fabrication of double-layer graphene
Alex Capecelatro**/UCLA	Orienting crystal growth using self-assembled monolayers
Craig Gorin*/Harvard University	Cesium promotion of styrene oxidation on single silver crystals
Josué Guerra*/Harvard University	An in vitro model for traumatic brain injury

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Daniel Harburg/Middlebury College	Aerogels for stabilizing and supporting fuel cells	
Aaron Magil/Carnegie Mellon	Environmental effects on the local density of states of	
University	CdSe quantum dots on a Au substrate	
Lori Sandberg/University of Wyoming	Microwave heating in microfluidic devices	
Yah (Laeticia) Sangne/Western New	L., L.;	
England College	Imbibition in customized systems of packed beads	
Patrick Stollenwerk/The Ohio State	Environmental effects on the local density of states of	
University	CdSe quantum dots on a Au substrate	
Anthony Vicari*/Harvard University	Fabrication of Bragg gratings using subwavelength-	
	diameter silica nanowires on a mesoporous silica	
	substrate	

^{*}Partially supported by Harvard College funds

The enhanced infrastructure provided by the REU/RET Site Program has allowed us to expand the program of professional development workshops, faculty seminars, and social and cultural activities that are designed to create community among participants and research advisors. These activities continue to include mentor training prior to the program start; weekly faculty-led research and ethics seminars; professional development workshops, including written and oral presentation skills workshops; large and small group discussions on applying to graduate school; and various athletic and social events during the summer.

One goal of our REU program is to develop essential skills in communicating effectively with scientists and the public. In collaboration with the Museum of Science, Boston, we hold a presentation skills workshop for REU students. During this workshop, students engage in discussions with Tim Miller and other education associates from the Museum of Science, Boston, on how to present complex scientific concepts. This format is very effective in increasing the confidence of these young scientists and engineers in discussing science with their peers and mentors. The workshop is followed by evening practice sessions in the week prior to the final symposium. A new component of our REU program is a weekly meeting to help students learn to read and write scientific papers. Students rated this component very highly, and we plan to continue this workshop in future years.

In addition to the end-of-summer research symposium, mentors are encouraged to seek out opportunities for students to participate in professional meetings. This early exposure to the professional life of an academic is important in encouraging young scientists and engineers to continue in academia. For example, Ms. Laetitia Sangne presented her work at the Fall meeting of the American Physical Society Division of Fluid Dynamics; several students will present at upcoming regional and national conferences.

Mentoring an REU student is a valuable professional development opportunity for a graduate student or postdoctoral researcher, allowing this population to explore effective models for project management. To enhance this experience for mentors, we have implemented a series of preparation sessions with REU mentors. New mentors participate in a series of luncheons in which faculty and other experienced mentors share strategies for mentoring undergraduate students, including planning a realistic project, modifying

^{**}Partially supported by Army Research Office under award #W911NF-04-1-0170

project goals, effectively managing time, and motivating students to work independently and as part of a team.

Outcomes. Since 2003, the NSEC has funded or partially funded 59 REU students. To date, 39% of these students are enrolled in MS/PhD programs in S&E, 29% are currently enrolled in undergraduate S&E programs, 12% are employed in S&E companies, while 8% are pursuing medical or law degrees, 3% are teaching at the K-12 level, and the remaining 8% are consulting or pursuing non-S&E careers.

Planned Activities. We plan to continue our program of activities for REU students and mentors, and will modify the program each year in response to formative evaluations.

10.4 Postdoctoral and Graduate Student Professional Development Activities

The NSEC based at Harvard has been involved in professional development of postdoctoral fellows since its inception. Sections 10.4.1–10.4.2 discuss ongoing opportunities for postdoctoral fellow and graduate student involvement in educational and professional development opportunities. In addition to the current NSEC-based activities describe below, graduate students and postdoctoral fellows are encouraged to participate in the newly developed professional development seminar series offer in spring of each year by SEAS (http://seas.harvard.edu/profdev), which addresses topics such as mentoring and project management, writing proposals and papers, and handling implicit biases. University-wide, postdoctoral fellows also have access to the professional development programs offered by the Office for Postdoctoral (http://postdoc.harvard.edu). Resources available include workshops on networking, academic interviewing, and responsible conduct in research. Additionally, postdoctoral fellows and graduate students who are REU mentors are also asked to participate in a series of mentoring and project management workshops in the spring.

10.4.1 Course and Seminar Development

Current Activities. In addition to the mentoring and professional development activities embedded in our other educational programs, graduate and advanced undergraduate students participate in AP298r, *Interdisciplinary Chemistry*, *Engineering and Physics*, an interdisciplinary graduate survey course of ongoing research at the Center. These activities are further discussed in *11*. *Outreach and Knowledge Transfer*.

10.4.2 Public Communication Internships at Museum of Science

Current Activities. In 2007, we instituted a Public Communications Internship (PCI) for graduate students and postdoctoral fellows led by education associate Tim Miller at the Museum of Science, Boston. In April 2008 and January 2009, 8 graduate students and postdoctoral fellows participated in the week-long internship. The workshop is designed to give participants an in-depth perspective on how museum personnel approach informal science education; participants then develop a "product," which can be a tabletop demonstration, a 20-minute talk for the Museum floor, or a video on their research.

Outcomes. To date, 3 videos, 4 presentations for the Museum of Science, and 2 tabletop demonstrations have been developed by graduate students or postdoctoral fellows. Videos are posted to YouTubeTM, and will be linked to our website. Additionally, former participants will help with upcoming Nanodays events at the Museum of Science.

Planned Activities. We plan to continue the PCI, and are offering a session in June for graduate students and postdoctoral fellows. Participants in the PCI have and will continue to give talks in other venues, including through Project TEACH activities (see above), Science Cafes (www.sciencecafes.org), and Science in the News (https://sitn.hms.harvard.edu/podcasting/)

10.5 Museum of Science, Boston (subawardee)

Carol Lynn Alpert, Director of Strategic Projects
Tim Miller, Nanoscale Science and Engineering Education Associate

10.5.1 Research Accomplishments and Plans

Public Engagement

The Museum of Science subaward is focused on producing robust and effective public engagement nanoscale science and engineering. We seek to expose a broad and diverse audience to the research work of the NSEC and to nanoscale science and engineering generally, and to develop best practices in outreach and education that can be shared among the larger research and informal science education communities, through the NISE Network, the NSEE, and other professional learning organizations. Over the past year we have deepened and expanded our pursuit of successful strategies pioneered in previous years, while prototyping several promising new initiatives.

Activities and Impact. NSEC Education Associate Tim Miller develops and delivers live presentations related to nanoscale science and engineering in the Museum's popular Gordon Current Science & Technology Center, three to five times a week. In 2008, Tim Miller delivered 160 live presentations to a total audience of 3700 Museum visitors, and produced three guest researcher events with NSEC investigator Kit Parker, and graduate students Naveen Sinha and Lisa Marshall. Tim delivered seven nano research science news stories to the Sci-Tech Today feature on New England Cable News, which reaches up to 15,000 viewers throughout New England, and delivered podcast versions of those stories to the Museum's iTunes channel, which has a subscriber base of 5,000.

In 2007, <u>Carol Lynn Alpert</u> wrote and directed development of The Amazing Nano Brothers Juggling Show, in collaboration with performers Dan Foley and Joel Harris, and this 40-minute stage production, which explores the structure of matter, nanoscale size and properties, and scanning probe microscopy has been seen by more than 9500 visitors during 55 performances in 2008. It is one of the most successful and popular Museum programs ever produced at MoS, and was cosponsored by the Center for Highrate Nanomanufacturing. The show has been so successful that we are commissioning an independent evaluation in 2009 in order to accurately assess what audiences are learning

from the show. We also plan to develop a traveling version of the show that can tour schools.

New in 2008, was a week-long series of events called NanoDays, that MOS sponsored in conjunction with the NISE Network. The event included demonstrations of nano phenomena, applications and research by NSEC graduate students, talks by NSEC faculty and graduate students, and a special talk and demonstration by IBM's Don Eigler, then on sabbatical at Harvard.

MoS and the Harvard NSEC also collaborated in an effort to help Twin Cities Public Television filmed scenes for two episodes of *Dragonfly TV Nano* at MoS and at the Harvard laboratories, with the participation of several NSEC graduate students. The programs air on PBS stations this spring, and each episode is viewed by more than one million people. The programs will also stream on the web and be downloadable to video iPods.

The MoS team also produced *Talking Nano*, a 6-DVD edited collection of presentations on nanotech research and societal implications. Talks by Harvard NSEC associates <u>George Whitesides</u>, <u>Eric Mazur</u>, Tim Miller, and Don Eigler, are included in the set, as well as a finely-produced video of *The Amazing Nano Brothers Juggling Show*. The DVD set, co-sponsored by CHN, received a "two-thumbs-up" review by Sir Harry Kroto in the Jan/Feb 2009 edition of *Materials Today*, and is being widely distributed through the NISE Net and talkingnano.net for school, classroom, professional development and home use.

Professional Development and Science Communication Training

The Public Communication Internship program for NSEC graduate students continued with two cohorts of students: session 3 in April 2008 and session 4 in January 2009. Six students participated this year. This program brings graduate students from the NSEC to the Museum for an intensive one-week practicum in communication, education, and outreach. Each participant completes a public communication project, which can be a video of their work or a live presentation before a Museum audience.

Tim Miller also offered a special workshop on science communication skills for 35 REU students visiting the NSEC in 2008.

In 2009, the Museum will be working with our Research and Evaluation Department to conduct formative evaluation of these professional development programs with the idea of not just improving them, but also sharing the curricula and techniques with other science museums working with research center partners and participating in the NISE Network.

11. OUTREACH AND KNOWLEDGE TRANSFER

The NSEC has strong partnerships with researchers from national laboratories, industry, and international institutions. During the past year, Center researchers worked closely with members of the Nanoelectronics Research Initiative (NRI) under a supplemental award to the NSEC aimed at ultrasmall electronics. The NSEC cosponsored a workshop in Basel, Switzerland on the Frontiers of Nanoscale Science and Technology (FNST) that brought together leading researchers from industry as well as many of our national and international collaborators. New international collaborators joined the NSEC and the successful visitor program continued that allows our postdoctoral fellows and graduate students to travel and work directly with our partners. These exchanges provide valuable educational and professional experiences. Several international delegations visited the Center, there were a number of talks given by industrial researchers, and the NSEC co-sponsored the local NanoTechnology Business Forum during the year. The NSEC also supported community-building endeavors through the postdoctoral fellow and graduate student coordinated research exchange seminars and courses. These activities are described in more detail below and the complete list of partnering institutions with the Center is shown in Table 6: Partnering Institutions.

NSF-SIA Supplement in Nanoelectronics

The NSEC maintains close ties with members of the Nanoelectronics Research Initiative (NRI). George Bourianoff, for example, has been a member of our External Advisory Committee. Meetings with members of the NRI during the past several years have identified areas of overlap between the NRI forward-looking 'research vectors' and ongoing research in the NSEC. When a supplement was announced by the NSF-SIA for



Figure 11.1. Shriram Ramanathan (*left*) and NSEC researcher, Gokul Gopalkrishnan (*right*) discussing their research efforts on oxide switches with members of the Nanoelectronics Research Initiative (NRI) at Harvard University, November 2008.

graduate student and postdoctoral fellow to NSF Centers in nanoelectronics, a successful supplemental proposal was submitted to the NSF to synthesize and characterize oxide nanostructures that was funded in 2008. Assistant Professor Shriram Ramanathan (Fig. 11.1), who came to Harvard from Intel, is one of the senior investigators involved in the

research. The goal of the research effort is to understand mechanisms governing phase transitions in oxide thin films and how they are affected by temperature and electric fields.

International Technology Roadmap for Semiconductors (ITRS) — Emerging Research Devices (ERD)

The International Technology Roadmap for Semiconductors (ITRS) is the fifteenyear assessment of the semiconductor industry's future technology requirements. These future needs drive present-day strategies for worldwide research and development among manufacturers' research facilities, universities, and national laboratories.

The Emerging Research Devices (ERD) Section of the ITRS evaluates new approaches from academic and industrial labs that could lead to devices that go beyond the ultimate scaling of CMOS technology. Robert Westervelt participated in the Emerging Research Logic Devices meeting in Montreux, Switzerland. The technologies considered range from one-dimensional structures such as nanotube and nanowire FETs, to single-electron transistors, to spin transistors — all part of the research of our NSEC. A lively discussion between academic and industrial researchers during the meeting about the merits and limitations of different types of devices provided an important connection between our Center's research and future nanoelectronics for the semiconductor industry.

Industrial Interaction and Technology Transfer

Several leading experts from industry visited the NSEC during the past year. Don Eigler (Fig. 11.2) from IBM-Almaden spent a sabbatical at Harvard interacting with members of the NSEC. Eigler presented a set of distinguished Loeb lectures in the Department of Physics and gave a number of insightful tutorial lectures such as in the NSEC Imaging seminar series. Other industrial scientists, such as Dan Angelescu from Schlumberger (Fig. 11.2) also gave talks for our students on their research as well as discussing other opportunities for collaboration. In fact, Schlumberger recently relocated their research laboratory from Connecticut to Cambridge to be in closer proximity to MIT and Harvard. Several of the NSEC faculty members are working closely with



Figure 11.2. Don Eigler (*left*) from IBM Almaden and Dan Angelescu (*right*) from Schlumberger speaking in the NSEC Imaging seminar series.

Schlumberger researchers on new microfluidic and sensor applications. Industrial researchers have also been invited speakers at the annual Frontiers in Nanoscale Science and Technology (FNST) workshops, including George Bourianoff (Intel), Yu-Ming Lin (IBM), Jun'ichi Sone (NEC), Gian Salis (IBM Ruschlikon), and David DiVincenzo (IBM Yorktown).

NSEC researchers also continue to work closely with industry on technology development and several patent applications have been filed in the fields of micromanipulator arrays, near-field laser antennas, novel nanostructured materials, oxide thin film switches, nanowire device fabrication, and microfluidic devices. The best technology transfer continues to be in the form of Center students and postdoctoral fellows trained in this interdisciplinary fashion for positions in industry and as part of new start-up company formation.

Visitor Exchange Programs

The NSEC has a visitor exchange program between Center universities and the national laboratories to share facilities and carry out collaborative research. The Visitors Program is managed by our Center coordinator to encourage collaborative research by supporting student travel. Leo Kouwenhoven oversees the student exchange with Delft, which has excellent facilities to make and test nanoscale structures as well as an outstanding graduate program. It is also possible for students to spend a few weeks or months visiting, to learn new skills and conduct research. Seigo Tarucha and Yasuhiko Arakawa look after similar visits with the University of Tokyo. Fabio Beltram from the National Enterprise for NanoScience and NanoTechnology (NEST) Pisa, Italy has visited the NSEC on numerous occasions and formed collaborations with researchers in the Nanoscale Building Blocks and Imaging at the Nanoscale Clusters. Lars Samuelson and Andre Geim have also become active collaborators with members of the NSEC. Samuelson is well known for his synthetic work in semiconductor nanostructures from Lund University in Sweden. Geim, from the University of Manchester, is a leading expert



Figure 11.3. (*Left*) Jiming Bao, an NSEC postdoctoral fellow, and <u>Federico Capasso</u> visiting Lars Samuelson at Lund University; (*right*) <u>Michael Stopa</u> and Felice Frankel talking with members of the RIKEN delegation from Japan.

in graphene thin-film research for future electronic application.

There were a number of visits by Center faculty, postdoctoral fellows and graduate students to use facilities and collaborate on research with scientists at other Centers and National Laboratories. Jiming Bao, a postdoctoral fellow working with Federico Capasso, visited the Lund University to collaborate with Lars Samuelson on the development of semiconductor nanowire for photonic device application (Fig. 11.3). Thomas Balder from the Delft University of Technology visited Harvard to work with Michael Stopa who has developed simulations to guide experimentalists like Thomas with their work on transport in quantum dot systems. A symposium was held in March 2008 to explore the use of parallel computing in scientific problems with NSEC researchers and scientists from RIKEN in Japan (Fig 11.3). A memorandum of understanding (MoU) was signed to continue these exchanges that are at the forefront of bringing parallel processing technology to scientific computation in the coming years. There have also been visits by graduate students from the Westervelt group to both Delft and Lund Universities where they worked with researchers to fabricate nanowire quantum dots of InAs and InAs/InP. Researchers from Lars Samuelson's group traveled to Harvard, in turn, to learn and perform transport measurements of these nanostructures using the custom-built scanning probe microscope developed in the Center.

Table 11.1 International Collaborators

Yasuhiko Arakawa	University of Tokyo, Japan
Fabio Beltram	National Enterprise for nanoScience and nanoTechnology (NEST), Pisa, Italy
Piotr Garstecki	Institute of Physical Chemistry Polish Academy of Sciences, Warsaw, Poland
Andre Geim	University of Manchester, UK
Leo Kouwenhoven	Kavli Institute of Nanoscience Delft University of Technology, The Netherlands
Eugenia Kumacheva	University of Toronto, Canada
Daniel Loss	National Center of Competence in Research Nanoscale Science, University of Basel Switzerland
Hideo Ohno	Tohoku University, Japan
Maria-Anita Rampi	University of Ferrara, Italy
Hiroyuki Sakaki	Toyota Technical Institute, Japan
Lars Samuelson	Nanometer Structure Consortium Lund University, Denmark
Seigo Tarucha	University of Tokyo, Japan

The NSEC has fostered collaborations with a remarkable group of international partners who are not only outstanding scientists but also leaders of pre-eminent research institutes for nanoscale science worldwide (Table 11.1). This is an important outreach activity supported by the NSEC, since much of the best research is done in Japan or Europe. We have seen directly that our researchers learn from our collaborators how to

make new structures and devices, how to conduct new experiments, and how to understand theoretically why a device or system works.

International Workshops

In January 2008, the NSEC co-sponsored the Frontiers in Nanoscale Science and Technology (FNST) workshop focusing on quantum information processing that was held in Basel, Switzerland (Fig. 11.4). The location of the FNST workshops rotates



Figure 11.4 Frontiers of Nanoscale Science and Technology (FNST) Workshop in Basel, Switzerland in January 2008.

among our partners with invited speakers selected to draw both national and international from the United States, Japan, and Europe. Over 140 researchers from industry, national laboratories, and academic institutions attended. Our NSEC provided student scholarships to graduate student researchers from the NSECs and other U.S. universities who applied and presented their work during poster sessions. Additional support for the workshop was provided by ICORP-JST, CINQIE-JST, and IT-MEXT [Japan]. The significant support from our international collaborators is reflected in Table 5 on leverage to the NSEC. The FNST workshop was the sixth international workshop since the beginning of the NSEC in 2001. Again this year, the workshop served to bring together the many postdoctoral fellows and graduate students who began collaborations through the visitor exchange program. The workshop is an opportunity to learn what progress has been made since those visits and explore new areas of exploration. The seventh international workshop is scheduled for May 29–31, 2009 at Harvard and will be devoted to recent advances in nanoelectronics, nanophotonics, and spintronics.

The Center also hosted several international groups during the past year including delegations from England, France, Germany, Italy, Sweden, and Switzerland. In March 2008, we hosted a delegation of Japanese students sponsored through the NSF/MEXT young scientist exchange program. Several graduate students, postdoctoral fellows, and junior faculty members (Fig. 11.5) from our Center, together with young scientists from Japan gave research talks. We had smaller group discussions and tours of the shared experimental facilities during the afternoon. There will follow visits from a delegation of

young U.S. scientists, including members from the NSEC that visited Japan in the Fall of 2008.

Industrial Partnership Workshop

In May 2008, NSEC members participated in the annual meeting of the Industrial Partnership Workshops (IPW) sponsored by Harvard's School of Engineering and Applied Sciences (HSEAS). The IPW is directed by Executive Dean Fawwaz Habbal and is aimed at strengthening external collaborations by facilitating mutually beneficial relationships between outside groups and HSEAS



Figure 11.5 <u>Jennifer Hoffman</u> speaking to the MEXT exchange group from Japan during their visit to the NSEC in March 2008.

interdisciplinary research groups. The workshop was on *Materials and Structures for Energy* and was heavily subscribed (Fig. 11.6). With nearly 200 registrants, a video and sound feed to a second room was set up. NSEC speakers included <u>Cynthia Friend</u>, <u>Hongkun Park</u>, <u>Shriram Ramanathan</u>, <u>Robert Westervelt</u>, and <u>George Whitesides</u>. Following the presentations and a networking session, there was a poster session with NSEC postdoctoral fellows and graduate students to allow for more detailed interaction between the NSEC researchers and attendees. The next Industrial Partnership Workshop is planned for May 8, 2009 on *Biosensors: Engineering Concepts and Medical Applications* (www.seas.harvard.edu/partnerships).



Figure 11.6. (*Left*) Cynthia Friend introducing Hongkun Park as an invited speaker and (*right*) interactions during lunch at the Industrial Partnership Workshop, May 2008.

Nanotech Business Forum

<u>Westervelt</u> worked with Chinh Pham (Greenberg Traurig, LLP) to initiate the NanoTechnology Business Forum which brings together leaders from local business, industry, government and academia for monthly networking meetings. The monthly



Figure 11.7. Chinh Pham (*podium*) and <u>Robert Westervelt</u> (*left of podium*) during a session at NSTI Nanotech meeting.

meetings have rotated to different venues in the Boston area including Harvard and M.I.T. Robert Westervelt has spoken ongoing activities about Harvard in nanoscale science at several of the meetings. The Nanotechnology Business Forum was a key factor, for example, in bringing together Rick Rogers School **Public** (Harvard of Health), Giannoula Klement (Children's Hospital), and Dale Larson (Harvard **Biophysics** Program), who have become collaborators on the research in

Cluster I on the hybrid CMOS/microfluidic systems with <u>Ham</u> and <u>Westervelt</u>. Scientists and business leaders from the Nanotechnology Business Forum have also been regular attendees at the annual Industrial Partnership Workshop (IPW), to learn about key developments inside the NSEC and more broadly at Harvard. Greenberg Traurig together with our NSEC supported a session at a recent the NSTI Nanotech Conference on Novel Tools & Devices for Nanoapplications. <u>Westervelt</u> spoke about ongoing work at the interface on nanotech and biology and <u>Capasso</u> discussed Center research in nanophotonics. The session and panel discussion (Fig. 11.7) attracted a large audience attending this prominent annual meeting.

Community Building

During the past year, the Center continued to host the Research Exchange seminar that was initiated and directed by NSEC postdoctoral fellows. The seminar is held bi-weekly at lunchtime during the academic encourage vear to **NSEC** postdoctoral fellows and graduate students to learn about The other's research. each Exchange seminar has blossomed into a venue where graduate students can obtain the advice of the postdoctoral



Figure 11.8. Tom Kelly from Imago speaking on Atom Probe Tomography at the Research Exchange luncheon.

fellows on preparation for oral presentation and then give their talk at the Exchange. On occasion, outside speakers are invited (Fig. 12.8) and the seminar is held at Harvard and MIT, emphasizing both locations of our NSEC activities in Cambridge.

With the realigned research activities, a major theme of new tool development has emerged. We also initiated a bi-monthly series of meetings for graduate students, postdoctoral fellows and faculty members involved in imaging and other new tool development (Fig. 11.2). These meetings, often involving leading industrial scientists, helped to promote the exchange of best practices and technical expertise among members of the NSEC.

In the Spring of 2009, the NSEC is sponsoring the academic course *AP298r: Interdisciplinary Biology, Chemistry, Engineering, and Physics*, which covers fundamental concepts in nanoscale research as well as possible applications in a series of lectures by twenty-two NSEC faculty members (Fig. 11.9). Topics for the course are

drawn from Tools for Integrated Nanobiology, NanoBuilding Blocks, and Imaging Electrons at the Nanoscale. The course includes tutorial lectures on modeling at the nanoscale and the use of electron microscopy for image analysis. A paper and oral presentation on one of the topics are required and the lectures are being transcribed by the students at a level appropriate for secondary teachers as a further extension of our outreach efforts. A dozen students are taking the course for credit and another fifteen researchers and staff members regularly attended the class as auditors. The lectures are available on the Harvard website.



Figure 11.9. <u>Joanna Aizenberg</u> giving her AP298r lecture.

Research from the NSEC, particularly work from Cluster 1. Tools for Integrated Nanobiology, has lead to low-cost sensors that address needs in low-income populations of the U.S. and in the Developing World. <u>George Whitesides</u> was the keynote speaker at the recent *Innovations for Global Health Symposium* (Fig. 11.10) organized by the Harvard Institute for Global Health (HIGH). The Symposium brought together academic researchers, prominent industrial scientists and, importantly, students who are now doing field work in Africa to meet the needs of this broader community.



Figure 11.10. George Whitesides giving the keynote address (*left*) and panel discussion (*right*) at the Global Health Initiative Workshop at Harvard in December 2008.

12. SHARED AND OTHER EXPERIMENTAL FACILITIES

The shared facilities are operated to encourage both hands-on research by experienced and qualified users, and as educational tools for students and researchers from other disciplines who can benefit from their use. A broad range of facilities teaches students the skills of nanofabrication, imaging, and synthesis that they will need after graduation, and opens new avenues of investigations for all disciplines. The shared experimental facilities play a special role in fostering interdisciplinary exchanges. The facilities are the natural meeting places where students from all parts of the Center learn from one another and share technical expertise.



Figure 12.1. Recently completed Northwest building (*left*) and the new Laboratory for Integrated Science and Engineering (LISE) building (*right*) at Harvard University.

New Laboratory Construction

Harvard University supported the construction of the new, 470,000 sq. ft. Northwest building (Fig. 12.1) that was opened for occupancy in the Summer of 2008. The building is, like other recent science buildings built on campus, not dedicated to any particular science department but will be used to foster interdisciplinary research and teaching efforts with initial concentrations in the neurosciences, bioengineering and biophysics; the latter areas have strong overlap with ongoing NSEC cluster research. The new Northwest building joins the recent 135,000 sq. ft. Laboratory for Integrated Science and Engineering (LISE), which opened in the Summer of 2007 (Fig. 12.1), as another new interdisciplinary space in the north Yard. Both buildings are creating a research environment that centralizes major experimental facilities and fosters cross-disciplinary research. An important programmatic element in these new buildings is common space to promote collaborative exchanges. The LISE building includes extensive vibration-free space that houses major cleanroom and nanofabrication facilities, advanced imaging laboratories, and facilities for materials synthesis. In the past year, there has been substantial renovation for NSEC-associated faculty space as well as further build out for newly arriving imaging and fabrication instrumentation. These state-of-the-art facilities are available to all researchers in the NSEC institutions but also nationally through the NSF/National Nanotechnology Infrastructure Network (NNIN).

Harvard University also supported the construction of a new building in the north Yard at 60 Oxford Street. The top two floors, along with one floor in the adjacent Engineering Sciences Lab (ESL) at 40 Oxford Street are home to faculty in Bioengineering. Asst. Professor Parker's laboratories, for example, are located in this new building where he carries out his collaborative work in the Tools for Integrated Nanobiology Cluster. The University has also recently completed major construction of new student training



Figure 12.2. Undergraduates working on their semester projects in the new 3D Printing and CAD Laboratories in Pierce Hall at Harvard University.

laboratories in bioengineering, computer aided design, and micropatterning (Fig. 12.2). These recent buildings and teaching laboratories will continue to draw the science community together, across traditional departmental boundaries and be spaces where researchers can interact in new common experimental and training facilities.

Integrated Management of Facilities and Technical Staff

In January 1999 Harvard announced the commitment to launch several new interdisciplinary research centers in the sciences. The faculty had identified a strong scientific and technological need for the understanding and development of mesoscale



Figure 12.3. Zeiss Libra 200 MC STEM being installed in LISE in February 2009.

materials and structures. This new challenge would facilities sophisticated for nanofabrication, synthesis, and growth (Fig. 12.3). The Center for Imaging and Mesoscale Structures (CIMS) was born from this vision. Halperin, Co-PI of NSEC, was the first Scientific Director of CIMS. Harvard University supports the Center for Imaging and Mesoscale Structures (CIMS) to support research and education in the area of nanotechnology and mesoscale science. A main mission of CIMS was the provision, operation and maintenance of complex facilities for imaging and fabrication. CIMS began to purchase equipment and hire technical staff as well as construct a second cleanroom in the basement of the Gordon McKay Laboratory. The management of the shared facilities at Harvard from CIMS, MRSEC and NSEC were integrated in 2002; the management boards of these Centers work closely together. Importantly, instrumentation for new CIMS facilities are open to all students, research associates, staff and faculty of the NSEC (regardless of institution), and to all NSEC

collaborators. This integration made CIMS the main source for centralized user facilities in the Oxford Street science campus. In September 2004, <u>Marcus</u> became the Scientific Director of CIMS. In April 2005, CIMS was renamed to the Center for Nanoscale



Systems and they launched their new website (<u>www.cns.fas.harvard.edu</u>). In January 2006, Eric Martin joined CNS from Avici Systems (North Billerica, MA) as the Technical Director (Fig. 12.4).

CNS has sixteen full-time technical staff members and the available instrumentation is organized in three thematic areas: Imaging and Analysis; Nanofabrication (including cleanroom operation); and Materials Synthesis. The complete list of instrumentation is given at: (www.cns.fas.harvard.edu/facilities/).

In February 2009, a Zeiss Libra 200KV monochromated, aberration corrected Scanning Transmission Electron Micoscope (STEM) arrived and is being installed in the LISE imaging suites (Fig. 12.3). The new Libra 200 STEM will have a resolution of 0.09 nm with analytical capability of energy-



Figure 12.4. Eric Martin, CNS Technical Director, showing the imaging facilities in LISE to a visiting Japanese delegation.

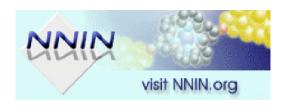
filtered spectroscopy and energy dispersive X-ray analysis (EDS). Two new field emission scanning electron microscopes have also been installed: a Zeiss Ultra, with ultimate imaging resolution of 1 nm and a Zeiss Supra for imaging and analytical work equipped with electron beam diffraction analysis (EBSD) and EDS. CNS also has a new Elionix STS-7000 E-beam system for nanometer electron-beam lithography. The Elionix system is complemented by a Raith 150 E-beam instrumentation as well as a JEOL JSM-7000F beam writer for high-current lithographic work. A new multi-beam FIB system, a Zeiss NVision 40, has also been installed that can be used for microfabrication, patterning and sample preparation.

CNS makes a direct, cost-sharing contribution to the NSEC through annual equipment acquisitions. The support and operation of the shared experimental facilities are the responsibility of CNS, with the only recharge to CNS from the NSEC in the form of user fees.

National Nanotechnology Infrastructure Network (NNIN)

UC Santa Barbara and Harvard University are two of the fourteen members of the

National Nanotechnology Infrastructure Network (NNIN) that began in March 2004. CNS is also responsible for managing the Harvard portion of the NNIN activity (www.nnin.org) that further reaches out to a national user base. The areas of focus at Harvard are soft lithography and the



assembly of nanoparticle and molecular electronics; theoretical simulations of electron states and transport in nanoscale systems. These areas have significant overlap with research in the NSEC.

Michael Stopa leads the coordination of the computational initiative in NNIN (Fig. 12.5). Stopa was previously at NTT in Japan and gave several seminars as part of the international exchange programs of the NSEC. Like the NNIN experimental program, NNIN/C is a multi-university initiative, the object of which is to establish a national computing resource that provides hardware resources and simulation tools dedicated to nanoscience research for the academic and industrial research communities. The software tools include commercial software packages for design and analysis, of nanometer scale devices as well as some of the latest academic advances in nanoscale modeling and simulation software. A workshop Synergy Between Experiment and Computation in Nanoscale Science was recently held (Fig. 12.5) that attracted over 100 participants, from other NNIN computational sites, across the nation, and from 12 countries. NSEC speakers at the workshop included Heller, Kaxiras, Marcus, and Whitesides.



Figure 12.5. <u>Michael Stopa</u> providing theoretical guidance to NSEC graduate researcher, Erin Boyd, on her experimental transport studies (*left*); <u>George Whitesides</u> speaking at the NNIN/C workshop on Synergy between Experiment and Computation (*right*).

Fettah Kosar (Fig. 12.6) oversees the operation of the Soft Lithography Foundary (SLF), which supports academic and industrial researchers and trains users on master fabrication and soft lithography. Fettah completed his Ph.D. in Bioengineering and Nanotechnology from the University of Washington in 2005. Before joining CNS, Kosar was a senior fellow in Paul Yager's group at UW, working on the design and development of a microfluidic point-of-care system for the rapid and on-the-field diagnosis of life-threatening infectious diseases in third-world countries. The University

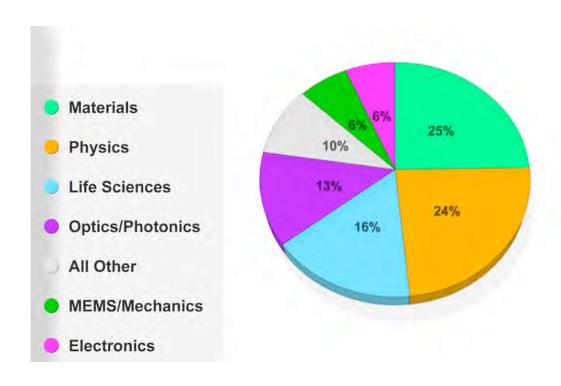


Figure 12.6. Fettah Kosar (*left, in blue lab coat*) teaching users in the soft lithography foundary; Noah Clay (*far right*) instructing a researcher in the clean room facilities in LISE.

of Washington is another of the NNIN nodes that specializes in soft lithographic work. CNS organizes soft lithography technical forums with other members of the network to disseminate and share technical knowledge and practical information on soft lithography across NNIN sites. Another recent addition to the senior staff of CNS is Noah Clay, who manages the nanofabrication facilities (Fig. 12.6). Clay's academic training was done at SUNY Oswego and Tufts University and he came to Harvard from the Goodrich Corporation where he worked making photon counting avalanche photodiodes.

User Statistics

The shared facilities are heavily subscribed with more than 1000 users from March 2008 through February 2009. Users came from many different institutions and varied technical fields. Below (Fig. 12.7) is statistical information of the shared facility users. Note that the Other category in the Institution Type chart includes small and large corporations, state and federal agencies, and international institutions. Also, most projects cut across many technical fields. In fact, it is part of the mission of CNS and NNIN to promote such interdisciplinary research. However, for the sake of tracking trends, users must select only one technical field when applying to the CNS/NNIN User Program.



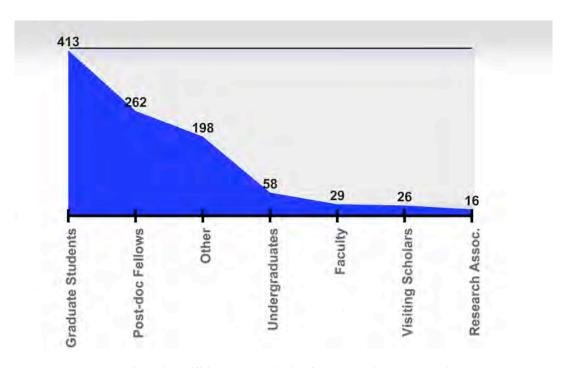
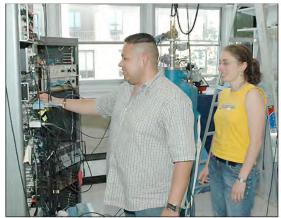


Figure 12.7. Shared Facilities user statistics from March 2008 to February 2009.

Student Training and Safety

Equally important to the acquisition of state-of-the-art instrumentation in the pursuit of our research program, is the availability of talented technical staff that provides training through regularly scheduled courses and hands-on laboratory instruction. The technical staff ensures that environmental health and safety procedures are followed and guidance is provided until researchers are certified as self-users. The staff also helps researchers develop new fabrication processes and measurements techniques, and upgrade equipment in response to changing research needs.

These cutting-edge instruments also are used in many of the Research Experience for Undergraduate (REU) and Teacher (RET) projects and, in many cases, are resources that are not available to many participants in these summer research programs back at their



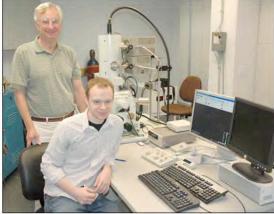


Figure 12.8. (*Left*) Sergio Gonzalez (REU, Univ. Texas, Pan American) working with his mentor, Erin Boyd; (*right*) Joseph Cox (REU, Eastern Nazarene College) and Visiting Professor John Free, during the summer research experience (REU) program.

home institutions (Fig. 12.8). This is an important illustration how the NSEC brings together talented researchers, who serve as mentors for undergraduates and teachers, technical staff with expertise, and essential (and often sophisticated) experimental facilities. Several REU students have returned to Harvard after finishing their undergraduate degrees as graduate students demonstrating the importance this activity has on their career choices.

Other Facilities

Center participants have access to other imaging, clean room, and synthesis facilities at MIT and UC Santa Barbara. The molecular beam epitaxy (MBE) facilities at UC Santa Barbara, for example, have long been among the premiere facilities available worldwide. In 2008, they completed installation of a new, interconnected 5-MBE chamber facility (Fig. 12.9) featuring: (1) A modified VG V80H MBE station for Asand Sb-based III-V semiconductors and As- and Ga-based metallic compounds, (2) a VG V80 for metal oxide growth, (3) a modified Gen-II EMOF MBE for metallic compound

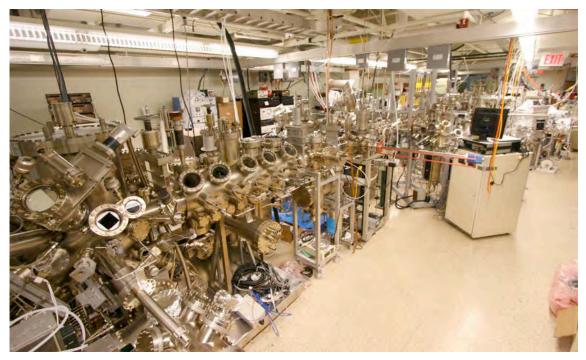


Figure 12.9. The new interconnected 5 molecular beam expitaxy (MBE) growth and characterization facility at UC Santa Barbara.

growth with atomic absorption and X-ray energy dispersive spectrometry for composition control, (4) a VG V80 MBE system for Ti-based metallic compounds, and (5) a VG V80H chemical beam epitaxy (CBE) growth system for As- and P-based III-Vs. These growth and deposition systems are complemented by a number of *in situ* surface characterization tools, including and Omicron variable temperature (50-750K) scanning probe microscope (STM and AFM), Auger and X-ray photoelectron spectroscopies, reflection high energy and low energy electron diffraction, and *in situ* current-voltage and capacitance-voltage measurements.

The NSEC has supported exchanges through the travel program by students who are experts in materials growth (UC Santa Barbara) to meet with students working in transport measurement (Cambridge). The National Laboratories also have excellent capabilities that help NSEC researchers, particularly those in micro-electromechanical structure (MEMS) fabrication facilities at Sandia (www.cint.lanl.gov). Westervelt serves on the Advisory Board of CINT.

Center participants benefit strongly from international collaborations with Delft University of Technology in The Netherlands, and the University of Tokyo, the Institute for Industrial Research and NTT in Japan. These institutions are world leaders in mesoscopic science and engineering. Leo Kouwenhoven has created a visiting program with Delft to exchange students and share facilities for collaborative research. Hiroyuki Sakaki and Seigo Tarucha are also coordinating visits with the University of Tokyo, the Institute for Industrial Research, and NTT for the design and fabrication, and testing of nanoscale structures (see also NSEC International Workshops in 11. Outreach and Knowledge Transfer, above). Our international collaborators have contributed to the travel support for student exchanges and to support joint workshops.

13. PERSONNEL

Administrative Structure

The Nanoscale Science and Engineering Center consists of twenty-seven senior investigators at four institutions (Harvard University; Massachusetts Institute of Technology; Museum of Science, Boston; and the University of California at Santa Barbara) with important collaborations with researchers from national laboratories, industry and international institutions. The NSEC offers dynamic educational programs for students and teachers at all academic levels and pursues unique opportunities to bring this research to the public through innovative programs with the Museum of Science in Boston. Harvard University is the coordinating institution for the NSEC. The administrative structure of the NSEC is shown below (Fig. 13.1).

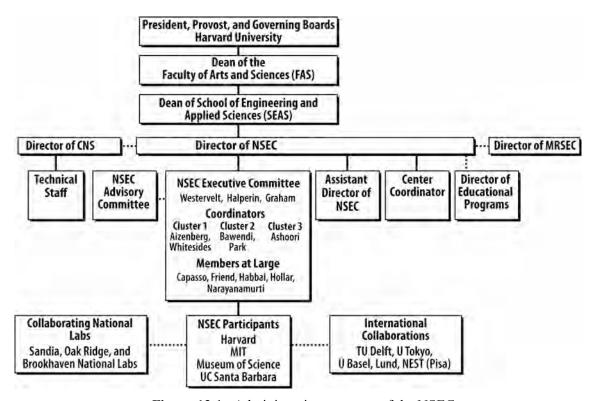


Figure 13.1. Administrative structure of the NSEC.

The Center is directed by the PI Robert Westervelt, who has a joint faculty appointment in the School of Engineering and Applied Sciences (SEAS) and the Department of Physics, and the Co-PI Bertrand Halperin, in the Department of Physics at Harvard. Decisions on research allocations and other major issues are made with the advice of the NSEC Executive Committee, shown in Table 13.1 (Fig. 13.2). Funding allocations are decided each year by the Executive Committee based on proposals for collaborative research and demonstrated progress in the previous year. New faculty members are added when their research overlaps with the goals of the Center and innovative projects, unrelated to the current program, may also be approved for funding

on a rapid and shorter-term basis as Seed Projects. The NSEC Executive Committee considers major capital equipment expenditures, evaluates staff appointments, and takes an active role concerning the allocation and budgeting process. In addition to the PI Westervelt, co-PI and the cluster Halperin, coordinators, members include Friend, Graham, Habbal,



Figure 13.2. NSEC Executive Committee.

<u>Hollar</u>, and <u>Spaepen</u>. All of the *ex officio* and at large members play key roles in support of the NSEC.

Table 13.1 Executive Committee

Joanna Aizenberg Raymond Ashoori Moungi Bawendi Federico Capasso Cynthia M. Friend Robert Graham Fawwaz Habbal Kathryn A. Hollar Bertrand I. Halperin Frans Spaepen	At Large Cluster 3 (coordinator) Cluster 2 (coordinator) At Large At Large, CCB Chair (04–07) NSEC Assistant Director Executive Dean, ex officio Education Director, ex officio NSEC co-PI Interim Dean, ex officio	Harvard M.I.T. M.I.T. Harvard Harvard Harvard Harvard Harvard Harvard Harvard	SEAS Physics Chemistry SEAS CCB and SEAS SEAS FAS and SEAS SEAS Physics SEAS and Physics CCB and SEAS
•			-

SEAS: School of Engineering and Applied Sciences

CCB: Chemistry and Chemical Biology FAS: Faculty of Arts and Sciences

<u>Frans Spaepen</u> is the Interim Dean of the School of Engineering and Applied Sciences (SEAS); it has recently been announced that <u>Cherry Murray</u> will join Harvard in July 2009 at the new Dean of SEAS. The NSEC is administered through Harvard's SEAS and benefits from the use of SEAS services (*i.e.*, purchasing and accounting) at no direct cost. <u>Fawwaz Habbal</u> is Executive Dean for Research and Planning in SEAS. He came to Harvard from industry and oversees the annual Industry Partnership Workshop (IPW) each spring. The NSEC annual meeting and advisory board have been held in proximity to the Industry Partnership Workshop. This timing takes advantage of presentations that are of interest to current and potential industrial collaborators.

Cynthia Friend (Fig. 13.3) serves as Associate Director of the Harvard MRSEC and is also an Associate Dean of FAS. She was Chair of the Department of Chemistry and Chemical Biology (CCB) from 2004–07. She is also the PI, along with Howard Stone, of the NSF-REU Site award in Materials Research that is jointly run with the NSEC, REU and RET programs. Friend plays a vital role advising senior University administrators on issues of gender and of importance to members of underrepresented



Figure 13.3. Cynthia Friend (center) talks with female Center postdoctoral fellows and graduate students at a reception following her gender equity discussion with these researchers.

groups in science and engineering. She was recently Co-Chair of the national workshop, "Building Strong Academic Chemistry Departments through Gender Equity," which provided recommendations for academic institutions and federal agencies.

There is an important relationship with the Center for Nanoscale Systems that has responsibility for the integrated management of the shared facilities. CNS is supported by Harvard University. Marcus became Scientific Director of CNS in September 2005; Halperin served as the first Scientific Director. Costs of technical staff and major instrumentation, all available to NSEC researchers, are borne by the University. This represents substantial leveraging of the NSF/NSEC support. CNS is also the managing institution for activities of the National Nanotechnology Infrastructure Network (NNIN) at Harvard. UC Santa Barbara is also one of the thirteen partner institutions of NNIN.

The NSEC Assistant Director is the senior non-faculty person who is responsible for

the Center's operation. They help supervise the staff, oversee programs and workshops, and manage the preparations of reports. A Center coordinator administers the Center's Visiting Program to help students, faculty and staff at different institutions collaborate through visits to operate shared facilities and carry out research.

<u>Kathryn Hollar</u> is the Director of Educational Programs in SEAS (Fig. 13.4). <u>Hollar</u> came from the Department of Chemical Engineering at Rowan University in Glassboro, NJ. She manages the



Figure 13.4. <u>Kathryn Hollar</u> (*right*) with <u>Howard Stone</u> (*left*), Daniel Rosenberg, and Amy Rowat following the Holiday Lecture, "From Bean to Bar: The Sweet Science of Chocolate," December 2008.

Center programs in education at all levels, and promotes outreach to public schools and the general public. <u>Hollar</u> works closely, for example, with the Museum of Science staff to adapt new laboratory results for the Current Science & Technology Center (MoS/CSTC) and as part of the NSF/Nanoscale Informal Science Education (NISE) Network. They work together to provide professional development tools through workshops for our undergraduates and K12 teachers. She is also coordinating the REU Site award with close partnerships to the Cambridge Public Schools, a majority minority school system. The NSEC makes an annual contribution for salary, but the largest portion of her support comes from the University.

Advisory Committee

An Advisory Committee, shown in Table 13.2, consists of leading figures in business and industry and the national laboratories, provides guidance to the Executive Committee, particularly in its efforts to expand and intensify links between the NSEC and industry.

Table 13.2. Advisory Committee

Kenneth Babcock Si Biosensors George I. Bourianoff Intel Corporation

Donald Eigler IBM, Almaden Research Center

Steven Girvin Yale University
Rachel Goldman University of Michigan

Harald Hess Howard Hughes Medical Institute

Paul L. McEuen Cornell University
Carmichael Roberts
John Rogers University of Illinois
Richard Slusher Lucent Technologies

Tom Theis IBM, T.J. Watson Research Center

Ellen D. Williams University of Maryland

The Advisory Committee serves as an external board concerning the importance and relevance of the Center's research and educational programs. The Advisory Committee also meets with our NSEC postdoctoral fellows and graduate students, offering advice and assistance in career development. The industrial members of the Advisory Committee are also helpful in establishing visits between Center researchers and industrial executives and research scientists to explore collaboration as well as applications of the Center's research.

Selection Guidelines and Procedures

The following guidelines are used in evaluating potential new Research and Seed Projects, major equipment purchases for Shared Facilities, and in the decisions to fund educational or outreach programs.

- 1. High-quality research with clear and concise scientific goals
- 2. Interdisciplinary nature
- 3. Originality; high-risk research with high potential
- 4. Relevance to existing or planned research groups
- 5. Career development for younger faculty
- 6. Promotion of innovative teaching, training and learning in materials science

Director's Reserve

Because of the ever-changing and fast-paced nature of scientific research, unexpected occasions to fund an exciting research idea, a new faculty member, or new equipment will often arise. Reserved funding is allocated to the Director's Fund so that these opportunities may be fully exploited. Funding of students is emphasized to foster their career development.

Administration of Center Visiting Programs and Outreach Activities

The NSEC supports visiting programs to help graduate and undergraduate students do collaborative work at the academic institutions; at the national laboratories, with researchers in industry; and with our international partners—the University of Technology at Delft, the University of Tokyo, NEST in Italy, the University of Basel, and Lund University (Sweden). The NSEC also supports activities such as the Research Exchange program that is organized by NSEC postdoctoral fellows and graduate students and meetings of NSEC cluster groups (Fig. 13.5) that promote a sense of community within the Center.



Figure 13.5. Bi-weekly meeting of the Research Exchange group, organized by NSEC postdoctoral fellows and graduate students; Prof. Marc Eriksson from the University of Wisconsin giving a special seminar to the NSEC postdoctoral fellows and graduate students.

14. NSEC PUBLICATIONS and PATENTS

- *Note:* ^a signifies research principally supported by the NSEC
 - ^b signifies research partially supported by the NSEC
 - ^c signifies research where NSEC Facilities were utilized
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- 10. **Parker, K.K.**, "Cardiac applications of thin film based tissue (MTF SA Node)," Harvard Case 3244, Case opened 5/23/2008.
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- 27. **Parker, K.K.,** "Method for generating funtionalized soft substrates micropatterning cells thereon," Harvard Case 3149, US Patent Application Serial Number 61/128,727, Filing date 9/24/2008.

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Patents Awarded

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- 2. **Whitesides, G.M.**, "Method and apparatus for gradient generation," Patent #7,314,070, issued 01/01/2008 (USA).
- 3. **Whitesides, G.M.**, "Method and apparatus for gradient generation," Patent #2002213423, issued 1/10/2008 (Australia).
- 4. **Whitesides, G.M.**, "Microfluidic systems including three-dimensional arrayed channel networks," Patent #7,323,143, issued 1/29/2008 (USA)
- 5. **Whitesides, G.M.**, "Cell patterning technique (formerly via an Elastomeric Mask)," Patent #2005248448, issued 3/13/2008 (Australia).
- 6. **Whitesides, G.M.**, "Valves and pumps for microfluidic systems and methods for making microfluidic systems," Patent #2002239823, issued 5/1/2008 (Australia)
- 7. **Whitesides, G.M.**, "Fabrication of metallic microstructures using exposed developed silver halide-based photographic film," Patent #7,399,579, issued 7/15/2008 (USA).
- 8. **Whitesides, G.M.**, "Microlens for projection lithography and method of preparation," Patent #7,403,338, issued 7/22/2008 (USA).
- 9. **Whitesides, G.M.**, "Device containing cytophillic islands that adhere cells separated by cytophobic regions," Patent #7,410,791, issued 8/12/2008 (USA).
- 10. **Whitesides, G.M.**, "Microfabrication technology microlens for projection lithography and method of preparation," Patent #1377853, issued 9/17/2008 (EU).

Patents Licensed

- 1. **Stone, Howard, A.**, "Novel Methods of Delivering Materials to Lungs," Case 2028, Filing Serial No. US 12/351,328, Date filed 1/9/2009, Patent pending; exclusively licensed.
- 2. **Stone, Howard, A.**, "Novel Methods of Delivering Materials to Lungs," Case 2028, Filing Serial No. US 12/351,328, Date filed 1/9/2009, Patent pending; exclusively licensed.
- 3. **Mazur, E.**, "Femtosecond laser-induced formation of submicrometer spikes on a semiconductor substrate, case 2536, application #11/196,929, issued 10/28/08.

Software Licensed

- 1. **Marcus, C.M.,** Jacob Aptekar, and Maja Cassidy, "Methods for making particles having long spin-lattice relaxation times" (filed in 2008), Patent Assignment 12/248,672.
- 2. **Marcus**, C.M., Jonathan Marmurek, Jacob Aptekar, "Telemetry through remote detection of nanoparticles" (filed in 2008), Patent Assignment 61/020,248.

15. HONORS AND AWARDS, 2007–2008

Joanna Aizenberg

Ronald Breslow Award for the Achievement in Biomimetic Chemistry, American Chemical Society (ACS), 2008

Fred Kavli Dinstinguished Lectureship in Nanoscience, Materials Research Society, 2008

Member of the Board on Physics and Astronomy, National Academy of Science (NAS), 2006–present

Member of the Board of Directors, Materials Research Society, 2006–present Member of the National Academies Committee on Biomolecular Materials and Processes, National Research Council (NRC), 2006–2008

Moungi Bawendi

Kavli Lecture in Nanoscience (Materials Research Society Fall Meeting)

Kenneth B. Crozier

Career Award, National Science Foundation, 2008

Cynthia M. Friend

Alexander von Humboldt Senior Research Award, AvH Foundation, 2007–2008 Hanse-Wissenschaftkolleg Fellowship, HWK Institute, 2008 Michelle Clayman Instutite Fellowship, Stanford University, Stanford, 2008 George Olah Award in Hydrocarbon Chemistry, American Chemical Spciety National Award, 2008/09

Arthur C. Gossard

The Al Cho MBE Award, International Conference on Molecular Beam Epitaxy

Bertrand I. Halperin

Selected as an Outstanding Referee for the journals of the American Physical Society, American Physical Society, 2008

Donhee Ham

Top 35 Young Innovator (TR35), MIT Technology Review, 2008

Jennifer E. Hoffman

Career Award, National Science Foundation, 2008

Marc Kastner

Member, National Academy of Science, 2008 Member, American Academy of Science, 2008

Charles M. Marcus

Member, National Academy of Sciences, 2008 Member, American Academy of Sciences, 2008

Eric Mazur

Millikan Medal, American Association of Physics Teachers (AAPT) Corresponding Member, Royal Academy of Arts and Sciences of the Netherlands Esther Hoffman Beller Medal, Optical Society of America (OSA) Fellow, Optical Society of American (OSA)

Venkatesh Narayanamurti

Invited Talk at Major Conferences, 2008

Member, Engineering Dean's Council, Cornell University, 2003–2010

Member, Engineering Dean's Council, Brown University, 2004–2010

Governing Board, Center for Integrated Nanaotechnologies, Sandia National Laboratory, 2006–2008

Member, Mork Family, Department of Chemical Engineering and Material Science Advisory Committee, University of Southern California, 2006–2010

Member, President's Council, Olin College, 2006–2010

Chair, NSF Advisory Panel on Light Source Facilities, NSF, 2007–2008

Member, Committee on International Security and Arms Control, National Academis, 2008–2010

Chair, NAE Nominating Committee, NAE, 2008–2009

Member, University Advisory Council, Semiconductor Research Corporation, SRC, 2008–

Hongkun Park

NIH Director's Pioneer Award, NIH, 2008–2013 Camille and Henry Dreyfus Teacher-Scholar Award, Dreyfus Foundation, 2008

Howard A. Stone

Bachelor Prize in Fluid Mehcanics, 2008 Brooke Benjamin Lecture in Fluid Mechanics, Oxford University, 2008

Robert M. Westervelt

Board of Advisors, Center for Integrated Nanotechnologies (CINT), Sandia National Laboratory, 2003–present

George M. Whitesides

Wieland Medal, Uiversity of Chicago, 2008

Outstanding Achievement Award in Nanotechnology, Ohio State Univ., 2008 Nanoscience Prize, International Scoeity for Nanosacle Sience, Computation and Engineering, 2008

Price of Asturias, Award in Science and Technology, Prince Asturias Foundation, Spain, 2008.