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## DoD's Multidisciplinary University Research Initiative (MURI) Program: Impact and Highlights from 25 Years of Basic Research

James Belanich Leonard Buckley Joan Cartier Michael Finnin Natalie Gluck Leon Hirsch Jenny Holzer Allison King James Ralston Pamela Rambow Felicia Sallis-Peterson Jeffrey Snyder Mark Taylor Stuart Wolf

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## Multidisciplinary University Research Initiative (MURI) Program: Highlighting Achievements

The Multidisciplinary University Research Initiative (MURI) Program is a Department of Defense (DoD) effort that supports academic research teams to conduct basic research addressing problems spanning science and engineering disciplines. The program was initiated over 25 years ago, and over 600 projects have been awarded since then. These projects are monitored by program managers (PMs) from DoD research offices (e.g., Army Research Office (ARO), Office of Naval Research (ONR), and Air Force Office of Scientific Research (AFOSR)). The standard MURI grant is for an initial 3-year period that is typically extended for a total of 5 years. The MURI program has regularly produced significant scientific break-throughs, and 25 of these projects are highlighted in this report.

DoD Instruction (DoDI) 3210.1, Administration and Support of Basic Research by the Department of Defense, addresses basic research and states that it is DoD policy that "basic research is essential to the Department of Defense's ability to carry out its missions because it is: (a) a source of new knowledge and understanding that supports DoD acquisition and leads to superior technological capabilities for the military; and (b) an integral part of the education and training of scientists and engineers critical to meeting future needs of the Nation's defense workforce." DoDI 3210.1 requires the Assistant Secretary of Defense for Research and Engineering (ASD(R&E)) to maintain a metrics program to measure and assess the quality and progress of DoD-funded basic research, and one element of that program is an independent technical review. This assessment, performed by the Institute for Defense Analyses (IDA), provides such an independent technical review.

To carry out this review, IDA developed metrics that could be applied across the government's historical records of the MURI grants for a quantitative analysis of the program. In addition, IDA conducted interviews with principal investigators (PIs) and PMs of MURI projects to obtain additional qualitative information for this review. Three principal dimensions were used for this assessment: scientific (publications, citations, and scientific significance indicated by a paradigm shift or furthering a domain), economic (patents and development of commercial technology), and military impact (development of military technology and follow-on military research efforts). Using the metrics along with qualitative input from project managers and subject matter experts (SMEs), the review team selected 25 projects to highlight for this report. The highlighted projects cover each of the three assessment dimensions: scientific, economic and military impact.

### **Highlighted Achievements**

Investment in basic research may be risky since it is an attempt to understand or achieve something that has never been done before. Over the years, the MURI program has provided grants for several projects that achieved first-time technical breakthroughs. Some of these singular achievements with far reaching consequences were as follows:

- Optical packet switching and all-optical label swapping (Bowers 1995), allowing for faster transmission speeds on the Internet and data networks
- Single walled carbon nanotube actuators and their use in optical switching (Dalton 1996), allowing for increased bandwidth in data transmission.
- Three-dimensional (3D) photonic band-gap in the microwave regime (Yablonovich 1996), allowing for more efficient radio antennas and enabling hybrid opto-electronic chips.
- DNA-based methods for rationally assembling nanoparticles into macroscopic materials (Schatz 1997; Mirkin 2000), allowing for new biological and chemical sensors.
- Design of nanoparticles to control the absorption of light (Halas 1999), allowing for targeted thermal effects to treat cancerous tumors
- Use of Bose-Einstein Condensation (BEC) as the active component of a sensor in a compact device (Kasevich 2000), allowing for more accurate timing and navigation devices.
- Use of extreme ultraviolet (XUV) frequency combs with sufficient power for measuring applications (Ye 2002), allowing for more precise measurements of distance and time.
- Multiple cycles of self-healing of composites for structural applications undergoing heat/strain cycles (White 2005), allowing for reduced maintenance requirements.
- Aluminum gallium nitride/gallium nitride (AlGaN/GaN) heterojunction bipolar transistors (HBTs) (Davis 1998), allowing for more efficient switching in semiconductors.

### **Quantitative Metrics**

The initial four metrics used for assessing MURIs in this analysis were publications, citations, patents, and derived patents. While these metrics were used to help identify MURIs to highlight, when assessed across projects, these metrics also provide insight into the overall performance of the MURI program. In general, MURI grants are scientifically very productive. The average MURI produces around 40 papers published in peer-reviewed journals. On average, each MURI grant collects over 1,000 citations on those 40 papers. Also, MURIs have been a source for many patents, even though not all MURI grants set out to produce patents. About a quarter of the MURIs produce patents, and these MURIs average approximately four patents each. Whether or not a patent is produced may reflect a relative difference in the focus of the PIs and their respective ambitions. It is likely that some PIs are driven more by the goal to discover basic scientific understanding, and others are more inclined to think entrepreneurially.

#### **MURI Program Structure**

Across all MURIs, there is a mix of highly focused and broad domain-based projects, and both types have been successful. There was a general difference across Services, where the Navy and the Air Force historically pursued a more focused style, with examples such as the use of silicon carbide (SiC) and gallium nitride (GaN) for high-speed communications, advanced radar, high-temperature electronics, and power control and switching (Davis 1998; Mishra 2001); the development of more accurate sensors (Kanade 1995; Kasevich 2000); materials that provide vehicles with improved blast protection (Wadley 2007); and improved design capability based on better understanding of radiation effects on electronics (Schrimpf 2005). Conversely, the Army was more likely to fund projects with broader objectives, with, examples such as an exploration of methods to fabricate structures on a nanometer scale (Whitesides 1987); the investigation of tunable optical polymers (Jenekhe 1999), which led to the development of polymers that sense explosive materials; the investigation of nanomaterials with innovative properties (Dalton 1996), which led to photonics applications that can increase speed and energy efficiency in communications technology; and investigation of novel capabilities of photonic crystals (Yablonovitch 1996), which led to improved imaging technology.

A structural aspect of the MURI program that is attractive to high-quality researchers is that the grants are large and stable. The size of the grant, which has grown to approximately \$1.4 million per year for 3 years, with a government option to extend the grant to 5 years, ensures a stable environment that gives researchers the freedom to take risks, be inventive, and explore. The multi-year stability allows a diverse research team to develop and mature into a quality team that can leverage each other's expertise. It can also be used to develop a critical mass of experts from more than one traditional research specialty to address complex domains. Examples of MURIs that brought together a critical mass of experts include Morse (1996), which led to the founding of the Institute for Collaborative Biotechnologies (ICB), and Schrimpf (2000), which led to the development of the Institute for Space and Defense Electronics (ISDE).

The PMs can have a significant impact on the success or complications of a MURI project. They are the individuals who come up with the initial set of topics against which project are proposed. In addition, PMs are the key government officials who monitor and guide the project through the years. Many of the PMs interviewed expressed philosophical agreement on what they consider to be the unique value of the MURI program: addressing the complex problems in science that require a diverse array of talents and expertise to make the next big step forward.

One difference between PMs was their status as active researchers. Some PMs are full-time research managers who are not actively conducting their own line of research but have extensive experience conducting research in the past. Other PMs are scientists who have their own active research programs in addition to managing research grants. The size of a PM's portfolio of grants

to manage seems to be based on whether he or she has active research programs. This difference also reflected a distinction between the Army and the other Services. The Army's PMs tended to have smaller portfolios of grants to manage while also conducting research themselves, while the Air Force and Navy PMs tend to manage larger portfolios but are less likely to have their own active line of research.

#### Summary

This analysis of the MURI program reveals that providing grants of adequate size and stability to work on complex research issues has attracted top-flight researchers who conduct productive research. They, in turn, produce a wealth of scientific, economic, and military achievements. These achievements are aided through the guidance provided by the PMs, who are usually the impetus for the research topic being included in the MURI program. The program managers also aid in the subsequent impact of the MURIs by recognizing the potential military significance of a discovery and then facilitating the exploitation of those achievements.

The MURI program has regularly produced significant scientific breakthroughs, as evidenced by the 25 highlighted MURIs analyzed in this study. One caution noted in the report was the inconsistency in documentation and acknowledgement of MURI funding. Data collection on the three dimensions covered in this report (i.e., scientific, economic, and military impact) on a regular basis would be useful to measure the impact of the MURI program. More regular documentation and acknowledgement of MURI achievements would help raise the visibility of the MURI program and allow it to receive full credit for the achievements that it enables.

The value of the MURI program, as evidenced by its diverse set of grants over the years, is its scientific, economic, and military impact. In this report, we highlight the 25 individual projects that were identified as highly successful MURIs through the selection process described previously. These highlighted projects include descriptions based on quantitative metrics and qualitative analysis.

## Synthesis and Study of Ultra-Small Structures and Devices Derived from Molecular Materials

This 1987 Multidisciplinary University Research Initiative (MURI) was one of the first MURIs. It was also one of the most important because it provided a key foundation for what has now come to be known as nanotechnology.

**Objective:** This MURI explored new paradigms for fabricating structures on length scales from nanometers to millimeters based on two revolutionary processes: self-assembled materials (SAMs) and microcontact printing ( $\mu$ CP).

Achievements: The fundamental accomplishment of this MURI was that it provided the first demonstration

of SAMs. The process involves the self-assembly of molecules called alkanethiols, which are sausage-shaped molecules with a sulfur atom at one end (see Figure 1). The sulfur atom sticks very well to a surface of gold or silver. Thus, if a thin film of gold is dipped into a solution of alkanethiol, the sulfur atoms attach to the gold and form a single molecular layer on the surface. Remarkably, the distance between the absorbed molecules is nearly the same as the diameter of the molecules, giving rise to a two-dimensional (2D) crystal of alkanethiol. The other end of the molecule can be tailored for a whole range of properties. This process, called functionalization, can produce surfaces that, for example, attract or repel water (hydrophobic or hydrophilic) or that



can affect adhesion, corrosion, or lubrication.

Figure 1. A Schematic Drawing of a Self-Assembled Molecular Material

This MURI also provided a second, very important innovation that is intimately connected with the SAMs. This innovation,  $\mu$ CP, involves creating a stamp made of an elastomeric material that is dipped in a solution of alkanethiols and pressed onto a gold surface (see Figure 2). The pattern on the stamp is replicated on the surface of the gold with a monolayer of alkanethiols and can form a template for any pattern that can be formed on

the stamp. The monolayer film ered by the

can be used as a photomask, and the gold not covered by the organic monolayer can be removed chemically. The alkanethiol layer can again be functionalized, and the resulting surface can be used for cell growth, biological and chemical sensing, and many other commercial and military applications. Furthermore, since the stamp is elastomeric and the gold can be deposited on curved and flexible surfaces, this technique has evolved into a technology called "soft lithography," which has been used to produce sensors, electrical circuits, and microfluidic circuits on a host of different surfaces for a large number of applications.



Figure 2. A Schematic of the Micro-Contact Printing Process

Synthesis and Study of Ultra-Small Structures and Devices Derived from Molecular Materials (1987–1993) Professor George Whitesides Department of Chemistry Harvard University

> Sponsor: DARPA Dr. Ira Skurnick

**Long-Term Significance:** The scientists at Harvard achieved two important breakthroughs in this MURI. The successful development of SAMs and  $\mu$ CPs has revolutionized many fields of science and technology (S&T), and these processes are currently being exploited for the fabrication of novel sensors and electronics. The seminal 1989 paper<sup>1</sup> by the Whitesides' group is their most cited paper, with over 3,000 citations. A recent review published in 2005,<sup>2</sup> also by the Whitesides group, documents the importance of this technology. This paper has received almost 3,000 citations. It is the second most cited of the Whitesides group's papers. Also remarkable is the explosion of citations for the work of the Whitesides group, in large part a result of this 1987 MURI. From the mid-1970s to the mid-1980s, the group typically had a few hundred citations per year but never more than 500. After the 1989 paper, the number of citations grew exponentially, reaching to over 10,000 per year in 2010.

Five key patents were also submitted during or closely following this MURI and were related to the two discoveries discussed previously. These five patents then generated an additional 1,300 derived patents. The Whitesides group itself has almost a hundred additional patents that are related to applications based on these initial discoveries, and several companies that have been formed are based on the commercialization of these patents. In fact, from the seminal work in this MURI, 16 companies have been formed and are working in areas that produce the hardware and technology for medical diagnostics. Only now are the full fruits of these discoveries being realized.

This MURI also supported a significant number of students and junior scientists: 5 undergraduates, 20 graduate students, 20 post-docs, and 5 visiting scholars, many of whom became professors or industrial researchers at major institutions.

Impact

- Provided a key foundation for the nanotechnology initiative
- First demonstration of selfassembled materials
- First demonstration of microcontact printing
- 16 companies created to produce sensors and novel electronics
- 5 key patents generated
- Over 1,300 derived patents

**Impact on DoD**: The impact of this basic research on DoD is extraordinarily diverse and significant. As a keystone for nanotechnology, this research revolutionized application areas ranging from electronics and sensors to microfluidics and tribology (i.e., friction, lubrication, and wear). Much of DoD's research in nanotechnology has its roots in the seminal work done in this MURI and the follow on research it enabled.

Understanding the important implications of this areas and vast potential, the Army created the Institute for Soldier Nanotechnologies (ISN) in 2002. The ISN's mission is to develop diverse nanotechnologies that can improve blast and ballistic protection, detect chemical toxins and detoxify them, provide physiological monitoring and automated medical intervention, and enable enhanced situational awareness.

<sup>&</sup>lt;sup>1</sup> Colin D. Bain et al., "Formation of Monolayer Films by the Spontaneous Assembly of Organic Thiols from Solution onto Gold," *Journal of the American Chemical Society* 111, no. 1 (1989): 321–335.

<sup>&</sup>lt;sup>2</sup> J. Christopher Love et al., "Self Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology," *Chemical Reviews* 105, no. 4 (2005): 1103–1169.

## Integrated Vision and Sensing Systems for Human Sensory Augmentation

The integration of vision algorithms with sensors to create low-power, low-latency, compact adaptive vision systems is necessary for augmenting the human sensory system and enabling sensory-driven information delivery. Potential military applications of such systems would be extensive (e.g., wearable smart vision systems to enhance situation awareness or headup display vision enhancement for low visibility conditions or telemedicine systems).

**Objective:** This Multidisciplinary University Research Initiative (MURI) explored four subareas of vision and sensing research: (1) smart optics, based on acoustoIntegrated Vision and Sensing Systems for Human Sensory Augmentation (1995–2000)

> Professor Takeo Kanade School of Computer Science Carnegie Mellon University

Sponsor: Office of Naval Research Dr. Thomas McKenna

optic tunable filter technology; (2) computational sensors that integrate raw sensing and processing using Very Large Scale Integrated (VLSI) technology; (3) neural-network-based saliency identification techniques for identifying the most useful information for extraction and display; and (4) visual learning methods for automatic signal-to-symbol mapping.

Researchers for this MURI were focused on improvements in three challenging areas: dynamic range (image intensity), tracking, and range (distance) estimation. The first challenge (dynamic range) is apparent any time one attempts to collect a photo in which a subject is indoors (dark conditions) but is backlit by a bright outdoors. Dynamic range describes the scale of light intensity over which the sensor is able to collect. Conventional sensors suffer limited dynamic range, meaning that they are confined to collecting either the dark region or the bright region of an image but not both simultaneously. Large dynamic range imagery allows the sensor to expose the dark subject and the bright background properly and simultaneously. As the researchers noted, such conditions are often faced in many military conditions (e.g., urban or indoors). The second challenge (tracking) has clear military significance. Autonomously tracking fast-moving objects across a scene stands to benefit applications ranging from autonomous navigation to targeting/tracking of high-speed projectiles, aircraft, and so forth. The final challenge (range) also presents clear military applications. Determining the distance to objects in a scene is a key information element for military engagements. Current ranging capabilities are dominated by laser range finders, which provide a very limited field of view (essentially one dimensional). Light detection and ranging (LIDAR) is an emerging two-dimensional (2D) ranging capability. The ability to collect range information from conventional 2D imagery is enticing since it is compatible with more conventional optical collection systems.

Achievements: Two existing technologies—acoustic-optic tunable filters and variable phase retarders—were combined to develop a system that dynamically extracts polarimetric and spectral information from an image at video frame rates. The researchers demonstrated improved discrimination of camouflaged objects, imaging in turbid (foggy) conditions, and terrain identification (see Figure 1).

Computational sensor research led to three developments. An adaptive range image computational sensor was designed and implemented in VLSI, and it achieved wide dynamic range. An attention-based optical tracking sensor to track targets moving very fast across an image/scene was designed and built. Based upon this sensor, an ultra-fast computational range sensor was developed for rapid triangulation of an object in a scene.



Source: http://www.ri.cmu.edu/.

Figure 1. Image with Potential Discrimination Difficulties Based on Similarity of Colors

Note for Figure 1: Both the armored vehicle and the long grass are similarly colored, but it is critical that a sensor is able to distinguish between them.

The MURI team developed and demonstrated algorithms for acquiring landmark models from sequences of images collected from a moving vehicle. This research included the development of techniques based on artificial neural networks (ANNs) for model learning and classification of landmarks. Algorithms were demonstrated on mobile robots in real scenarios. Artificial evolutionary search principles were applied to a variety of challenging areas, such as complex 2D maze navigation, recognizing faces at a distance, and three-dimensional (3D) matching and world modeling.

**Long-Term Significance:** This MURI targeted improvements in the full sequence of imagery-based information, from optical collection/sensing to imagery processing and information extraction. Rapid exploitation of optical imagery/information is critical in the conduct of military operations.

The smart optics research sought to collect spectral and polarimetric optical data dynamically. Dynamic is the operative word when compared to existent capabilities. The ability to collect these two forms of optical data at video frame rates may enable new

capabilities in identifying objects (terrain, vehicles, humans) in complex scenes where camouflage, concealment, and deception are rendered less effective. This capability could benefit the identification of hostile elements attempting to hide and the identification of friendly forces using covert methods of communicating their location unbeknown to the adversary.

The computational sensors work improved the readout/processing of imagery at the sensor. This growing application area stands to benefit military and civilian applications. The rapid, near-simultaneous collection and processing of optical imagery will speed up the acquisition of optical information about a scene.

The research from MURI resulted in 10 patents and approximately 90 derived patents. Also, the MURI team produced 31 publications that generated 3,529 citations.

**Impact on DoD:** The significance of this MURI to core capabilities of the U.S. military is fundamental. Just as DoD's investment in night vision enabled the capability that

#### Impact

- Developed revolutionary new optical-computational methods for image processing and analysis that contributed to robo-soccer championship win
- Face-detection work extended in a Defense Advanced Research Projects Agency (DARPA) program

allowed U.S. Army to state "We own the night." DoD has a significant need to enhance human vision sensory capabilities in a wide range of environmental conditions. This type of research will lead to a new era of perception advantage by U.S. Soldiers in the future (e.g., tracking individuals moving in crowds or detecting minute changes in scenery that could be implications of an improvised explosive device (improvised explosive device (IED)) placement).

## Multidisciplinary Optical Switching Technology (MOST)

Although semiconductor lasers and fiber-optic transmission media had been established in the 1970s and 1980s as superior technologies for the transmission of wide-bandwidth data streams, the fact remained that all of the data switching and control were accomplished in conventional electronics. The conversion from photons to electrons and back wastes energy and reduces the speed of transmission. This limitation became even more severe as fibers became capable of transmitting carriers of several different frequencies simultaneously (i.e., wavelength-division multiplexing). The time and system complexity required for repeated



demodulation of each carrier, application of data control and switching, carrier regeneration, and remodulation of the data stream soon became a bottleneck in the application of optics to long-haul wideband communications.

**Objective:** In recognition of this practical obstacle, a Multidisciplinary University Research Initiative (MURI) was established in the mid-1990s at the University of California, Santa Barbara to focus on developing optical technology as a means for controlling and switching the optical signal carriers directly, without need for repeated reduction to baseband electronic signals.

From 1995 to 2001, the MOST Center was able to focus the efforts of a wide range of optical, electronic, and network technology researchers and developers on the key issues related to the optical switching of time and frequency multiplexed wideband data streams. The unique advantage of the MURI-type organization was the ability to foster close and continuing cooperation among these researchers while maintaining their orientation toward the technologies underlying optical switching (see Figure 1). This illustrates a key advantage of MURIs: to direct efforts of a wide range of disparate technologists toward a specifically identified common goal.

Achievements: Some of the specific technology achievements—all related to the fundamental goal of supporting fully optical data control and quitching



Source: Bowers, John E. 2002. *Multidisciplinary Optical Switching Technology (MOST)*, Final Report: August 1, 1996–December 31, 2001. Santa Barbara, CA: University of California at Santa Barbara.

Figure 1. MOST Center's Multidisciplinary Focus on Optical Switching

fully optical data control and switching—include the following:

- *Three-dimensional (3D) photonic circuits.* These circuits were primarily enabled by the development of wafer-bonding technologies that allowed separately processed optical wafers to be assembled into multi-level optical structures. The resulting optical devices include waveguide couplers and multiplexers for transmitting or receiving ("adding or dropping") specific wavelength-division multiplexed carriers to a common fiber transmission line.
- *Electronically tunable filters.* To implement wavelength-division multiplexing, it is necessary to be able to separate specific laser wavelengths at will. Thus, it is critical to be

able to integrate tunable filters into optical switching circuits and larger scale optical networks.

- *Optical packet switching and all-optical label swapping.* Data packets, in addition to their data payload, incorporate a header label that defines the packet's origin and address locations. Techniques were developed that allowed data packets to be switched and readdressed, using all-optical techniques.
- *Ultra-fast optics*. Because instantaneously ultra-wideband optical pulses have pulse widths in the femtosecond range, they are too fast to be processed efficiently, even by the best optoelectronic logic elements. To circumvent this limitation, techniques were developed to disperse the ultra-short pulse spatially into individual narrow band components, which could then be successfully processed.
- *Double-heterostructure bipolar transistors in indium phosphide (InP).* The development of transistors with very high maximum operating frequency, although not a unique requirement of optical switching, pushed the limits of its day.
- Asynchronous transfer mode (ATM) switching using all-optical techniques. This achievement was the result of the MOST Center's focus on the next-generation communication optical switches.

**Long-Term Significance:** The economic implications of these advances in switching have been immense—faster communications with greater energy efficiency are now being applied in the commercial world. In April 2009, an international research consortium demonstrated all-optical signal processing on a siliconbased device at speeds of more than 100 Gb per second. Not only did these MURI researchers prove that ultrafast communication was possible on such a device, but they also demonstrated that all-optical data communication was practical.

#### Impact

- Increased speed of transmission of optical communication systems
- Increased communication bandwidth through use of multiple light frequencies
- Increased energy efficiency of optical networks
- Two start-up companies (Calient and Agility Communications)

Two startup companies were created in part as a result of the MOST Center:

- Calient (<u>http://www.calient.net/</u>) was created by Professors John Bowers and Daniel Blumenthal to commercialize optical switch technology for telecom applications. Several researchers who obtained advanced degrees under MOST are now part of this organization, which continues to produce state-of-the-art switches.
- Agility Communications was created by Professors Larry Coldren and Greg Fish to commercialize tunable laser technology for a wide range of applications, including communications, sensors, and biological monitoring. In 2005, Agility was purchased by JDS Uniphase Corporation (<u>http://www.jdsu.com</u>).

The research from this MURI resulted in 12 patents and 198 derived patents. Also, the MURI team produced 105 publications that generated over 3,300 citations. In addition, it support 17 graduate students and 10 post-doctorate fellows.

**Impact on DoD:** The advances made in commercial communications will also be of profound benefit to the U.S. military. DoD leverages this commercial technology for its own high-speed networks for communications, security, and tactical support. This technology area is one in which the commercial success of the United States forms a significant basis for its military effectiveness. Information superiority is based on a global information distribution network that, in many respects, was built on technology that has its roots in the technology developed by this MURI. The United States has a fundamental defense requirement to hold the leading edge of this technology.

## Multivariable Control, Simulation, Optimization, and Signal Processing for the Microlithographic Process

The continuing need for alternative techniques in microlithography addresses issues such as advancing Moore's Law, deposition on large or oddly shaped substrates, and removing lithography as a bottleneck in semiconductor manufacturing.

**Objective:** This Multidisciplinary University Research Initiative (MURI) advanced the art of microlithography in the application of multivariable control, simulation, optimization, and signal processing techniques to the microlithography sequence. In addition, a new technique called molecular transfer lithography (MxL) was developed. MxL bonds a water-dissolvable template that is precoated and precured with resist onto a wafer Multivariable Control, Simulation, Optimization, and Signal Processing for the Microlithographic Process (1995–2000)

Professor Thomas Kailath Department of Electrical Engineering Stanford University

Sponsor: Air Force Office of Scientific Research Dr. Marc Jacobs

and then dissolves away the template to reveal the pattern in the resist.

Achievements: MxL is a new class of printing strategies for manufacturing microstructures and nanostructures developed by the MURI team. It is a non-imprint, non-photolithography process used for applications involving large area, conformal printing at low cost and high throughput.

MxL involves coating a water-dissolvable template with a polymer resist and then bonding the resist to the target substrate as if it were an adhesive. The adhesion process is initiated by applying a small amount of heat to bond the resist to the substrate. Afterwards, the template is washed away in water to form the pattern on the substrate in the polymer material.<sup>1</sup> See Figure 1.



Water-Dissolvable Template Film with Dry Resist

Adhesion Operation with Tool

Source: Schaper, Charles D. 2010. "Automating Molecular Transfer Lithography at 25nm on 200mm Wafers Including Site-Remote Coating of Resist on Dissolvable Templates." *Proceedings of SPIE* 7637 (April): 73670U-2.

#### Figure 1. The Transfer Procedure of Bonding a Dry Film Resist Coated Polyvinyl Alcohol (PVA) Template onto a Substrate Using an Adhesion Operation and Then Dissolving the Template Away in Water

Existing semiconductor infrastructure is used for fabricating master templates to be used in the printing process. The water-soluble polymer templates are fabricated by spin casting a PVA film-forming solution to replicate surface patterns.<sup>2</sup> The templates are useful not only for pattern formation, but also for materials transfer printing, employing a low-cost, convenient, biocompatible chemical approach to high-resolution processing.

Initially, MxL was adapted for use on standard contact aligners, replacing the quartz photomask with a water-soluble polymer template. MxL worked in conjunction with existing patterning/ exposure tools to lower manufacturing and capital costs and removed or reduced critical

<sup>&</sup>lt;sup>1</sup> Charles D. Schaper, "Automating Molecular Transfer Lithography at 25nm on 200mm Wafers Including Site-Remote Coating of Resist on Dissolvable Templates," *Proceedings of SPIE* 7637 (April 2010): 73670U-1–73670U-9.

<sup>&</sup>lt;sup>2</sup> Charles D. Schaper, "Water-Soluble Polymer Templates for High-Resolution Pattern Formation and Materials Transfer Printing," *Journal of Micro/Nanolithography, MEMS, and MOEMS* 3, no. 1 (2004): 174–185.

technical problems associated with imaging tools (e.g., depth of focus, resolution, reflectivity, and contamination). The MURI work resulted in an improvement of the in-line throughput of stepper/scanner technology by a factor of 3 to 6, while significantly cutting the cost of the optical imaging tool. MxL is capable of large area patterning to substrates greater than 300 mm.

MxL has fewer steps than imprint lithography, which lowers costs and increases throughput. Imprint lithography involves four major steps: coating the substrate with resist, contacting the template to the resist, curing the resist, and separating the template from the resist. In contrast, MxL involves only two major steps: contacting the template to the substrate and dissolving the template in water. The MxL approach eliminates the coating step, which is important because it eliminates the need for the fabrication facility to handle and control wet resist materials, replacing it with a dry patterning procedure.<sup>5</sup> In addition, the MxL process has low defect generation because the template is dissolved away rather than being physically separated from the substrate as in imprint lithography and contact photolithography.

**Long-Term Significance:** Transfer Devices, Inc. (TDI) was formed in 2004 to capitalize on the MxL process. It is currently led by one of the original MURI researchers, Dr. Charles D. Schaper, and has significant intellectual property (IP) for the process of transfer lithography. TDI currently offers a high-throughput, automated nanolithography tool that does MxL processing, using resist-coated watersoluble templates to produce sub-50-nm features over largearea substrates in less than 1-minute cycle time.

MxL is now a commercial, low-cost manufacturing technology that has advanced the capability to manufacture nanopatterned devices for a wide range of commercial applications including integrated circuits (ICs), solar wafers, displays, data storage, and microelectromechanical systems (MEMS). Today, TDI designs and produces novel nano-



- Developed the new microlithography technique MxL
- Reduced costs and increased production rate than previous lithography process
- Increased throughput of stepper/scanner technology
- One start-up company, Transfer Devices, Inc., was formed

lithography capital equipment and functionalized soluble templates for innovative display, semiconductor, and energy applications.

The research from this MURI resulted in 4 patents and over 250 derived patents. Also, the MURI team produced 33 publications that generated over 931 citations. In addition, five graduate students completed their dissertations through the support of this MURI project, an indication of how it helped to train new scientists who will become the technologists sought by U.S. firms that wanted to maintain the leading edge.

**Impact on DoD:** The importance of this work to DoD is profound. DoD relies on very specialized chips that have to be made in local semiconductor foundries at state-of-the-art dimensions (e.g., 25 nm or less). This challenge has proven to be considerable since almost all of the conventional top-down lithographic foundries are not in the United States. The new technique of MxL developed in this MURI and continued by TDI enables the fabrication of these specialized chips in the United States at reasonable cost.

<sup>&</sup>lt;sup>3</sup> Charles D. Schaper, "Automating Molecular Transfer Lithography at 25nm on 200mm Wafers Including Site-Remote Coating of Resist on Dissolvable Templates," *Proceedings of SPIE* 7637 (April 2010): 73670U-1–73670U-9.

## An Acoustic Hemostasis Device for Advanced Trauma Care

Methods to stop bleeding quickly are important to the military, and this project developed the theoretical understanding of using focused ultrasound to arrest bleeding from battlefield trauma in an innovative manner (see Figure 1). The energy from ultrasound can pass through living tissue without harming it but can also be focused to induce blood clotting at a specific point. By using multiple transducers in an array focused on a specific point internally, the device can produce an intense acoustic effect on blood flow to induce clotting.



Source: Crum, Lawrence et al. 2004. Acoustic Hemostasis and Hemorrhage Control in Combat Casualty Care. Seattle, WA: Center for Industrial and Medical Ultrasound, University of Washington, and Oxford, MS: National Center of Physical Acoustics, University of Mississippi.

#### Figure 1. Demonstration of Successful Application of Image-Guided HIFU for Vessel Occlusion

Note for Figure 1: In the top image (A), a hemorrhage is identified. In (B), the HIFU is applied to the targeted location. In (C), the blood vessel supplying the region is occluded.

**Objective:** This Multidisciplinary University

Research Initiative (MURI) addressed the physical properties of non-linear pressure waves from ultrasound and the biological processes whereby blood clotting can be induced. In addition, it determined the effects of sound waves of particular frequencies and amplitude on different types of human tissue so the appropriate effects can be accomplished.

Achievements: This MURI conducted *in vitro* and *in vivo* studies to determine the acoustic power requirements for identifying the location of internal bleeding and to induce blood coagulation through acoustic hemostasis. It led to a better understanding of the physical mechanisms of high intensity focused ultrasound (HIFU), which can be used to image internal biological structures at lower amplitudes and produce enough acoustic energy to cause cavitation and thermal effects that produce biological effects, such as hemostasis, at higher amplitudes.

Based on the studies of the physical mechanisms of acoustic energy and the biological features of living tissue, researchers were able to create HIFU devices that were capable of imagery and therapy (e.g., hemostasis). Using HIFU devices of various designs and capabilities, researchers were able to test biological mediums to develop models to image internal structures with greater detail and to predict the physiological outcomes (cessation of bleeding, thermal effects) of HIFU use.

Based on this line of research, Dr. Crum won the Acoustical Society of America's Gold Medal in 2013 for the discovery and invention in physical and biomedical acoustics and for leadership in acoustics worldwide.

**Long-Term Significance:** This line of research has continued in applied medical research programs by the Navy, the Army, and the Defense Advanced Research Projects Agency (DARPA). Specifically, a DARPA project (2007–2011), during which prototypes of devices were developed

An Acoustic Hemostasis Device for Advanced Trauma Care (1996–2001)

Professor Lawrence Crum Center for Industrial and Medical Ultrasound Applied Physics Laboratory, University of Washington

Sponsor: Office of Naval Research Dr Jeannine Majde-Cottrell Dr. Stephen Ahlers that consisted of cuffs that could be wrapped around an arm or leg to detect internal bleeding with lower power, focused ultrasound and then acoustically induce hemostasis with HIFU at the point of internal bleeding.

Functioning prototypes that were successful in identifying internal bleeding and stopping blood loss were developed. However, the DARPA program goal set specific size/weight requirements so that it would be man-portable and could be deployed with a medic. While the functional goals of detecting and stopping bleeding within 30 seconds were met, the device size/weight goal of the program was not attained. Future efforts to reduce the size and weight of the device to meet field-portable requirements are expected.

In addition to hemostasis, the principles developed through this MURI have been used for cancer treatment (i.e., destroying tumors). The technology has been successful in identifying the exact location of tumors and ablating the tumors without incisions or radiation.<sup>1</sup>

The research from this MURI resulted in 7 patents and over 300 derived patents. Also, the MURI team produced 55 publications that generated 1,893 citations. In addition, this MURI supported 11 graduate students and a post-doctoral fellow.

Impact on DoD: Blood loss is a common cause of death on

the battlefield because of a lack of access to a facility that can control bleeding. The principles and techniques developed in this MURI demonstrated the possibility of a single device that would be capable of identifying internal bleeding at a specific point within a person's body and then halting that bleeding through the use of focused ultrasound. It is expected that the research performed in this MURI will enable the production of a portable system through which a medic can identify internal bleeding and then halt blood loss. This advancement would significantly improve the chances for successful recovery of Soldiers who suffer battle injuries.

#### <sup>1</sup> For additional information on the use of focused ultrasound technology, see "Focused Ultrasound Foundation: Overview," http://www.fusfoundation.org/the-technology/overview.

**Imp**act

- Developed a novel procedure to induce acoustic hemostasis
- Developed prototype for initial demonstration of capability
- Technology based on MURI is being used for cancer tumor ablation

## Materials and Processing at the Nanometer Scale

Electro-optic (EO) materials are able to change their refractive index with an applied electric field. EO modulators are devices that contain EO materials and can be used for controlling the power, phase, or polarization of a laser beam with an electrical control signal. EO modulators thus convert electrical data into optical information. Originally, EO modulators used inorganic crystal materials such as lithium niobate (LiNbO<sub>3</sub>)and potassium dihydrogen phosphate (KDP). Applications of these devices include high-speed optical switching technology, communications and radar systems, and electronic countermeasures.

Materials and Processing at the Nanometer Scale (1996–2001)

Professor Larry R. Dalton Department of Chemistry University of Southern California

Sponsor: Air Force Office of Scientific Research Dr. Charles Lee

**Objective:** This Multidisciplinary University Research Initiative (MURI) explored the development of nanostructured materials to achieve new and enhanced material properties for photonics applications. In particular, it explored the use of nanoscale dendrimers to achieve electronic isolation and directed energy/charge transport. A dendrimer is a large, synthetically produced polymer in which the atoms are arranged in many branches and sub-branches radiating out from a central core These novel dendrimer materials can then be used to develop improved EO modulator materials, light harvesting and optical amplifier materials, high-density electronic memory materials, light-emitting diode (LED) materials, and two-photon lasing materials. Incorporating EO organic chromophores into the core of the dendrimer eliminates quenching of macroscopic EO activity by intermolecular (chromophore) electrostatic interactions.

Achievements: The researchers supported by this MURI pioneered the development of dendrimers for electronic and optical applications. Important accomplishments include the first demonstration of single-walled carbon nanotube actuators and their use in optical switching. Polymer nanospheres were used to demonstrate high-density erasable optical memories and nanoscale chemical reactors for fuel-cell efficiency improvements. Probe-lithography was used to prepare prototype molecular electronics devices on self-assembled monolayers. A self-assembly method for the large-scale fabrication of three-dimensional (3D) photonic bandgap crystals was also demonstrated. Production and functionalization of polymer nanospheres for many applications were explored. Highlighted below is the development of polymer materials to improve the performance of EO materials.

Several promising new EO dendritic materials systems were developed under this MURI. The MURI team developed a new type of dendrimer structure that contains an organic chromophore (i.e., a group of atoms that absorbs light at a specific frequency). The addition of chromophores into the dendrimer structure gives the molecule many desirable properties (see Figure 1).<sup>1</sup>

Results showed that the EO activity (response rates when exposed to a changing electric field) for the dendritic chromophore polymer was a factor of three larger (at telecommunications wavelengths) than that of the best inorganic crystal material (lithium niobate) that was in use for EO applications at that time.<sup>2</sup> In addition, the polymer material displayed better thermal and photochemical stability of the EO activity.

The new polymer material was subsequently used in the design and fabrication of high-speed, ultra-low drive voltage EO modulators. The EO modulator devices developed by this MURI team were characterized by drive voltage requirements of less than 1 V and converted electrical data into optical information at rates exceeding 110 GHz. Similarly high data rates had been

<sup>&</sup>lt;sup>1</sup> Hong Ma et al., "Highly Efficient and Thermally Stable Electro-Optical Dendrimers for Photonics," *Advanced Functional Materials* 12, no. 9 (2002): 565–574.

<sup>&</sup>lt;sup>2</sup> Larry R. Dalton, "Organic Electro-Optic Materials," *Pure Applied Chemistry* 76, nos. 7–8 (2004): 1421–1433.

reported for other polymer-based devices before 2000, but those systems required much higher drive voltages, which affected noise levels and limited the signal gain.<sup>3</sup> Operation at low drive voltages is necessary for compatibility with the fastest electronic components.



Source: Hong, Ma et al. 2002. "Highly Efficient and Thermally Stable Electro-Optical Dendrimers for Photonics." Advanced Functional Materials 12 (9): 569.

#### Figure 1. Three Examples of Dendron-Modified Chromophore Polymers

**Long-Term Significance:** Organic EO materials are much simpler to fabricate and process than inorganic crystalline materials, which require electric poling or the growth of large single crystals. Thus, device cost can be lowered considerably. Conformal and flexible devices that cannot be achieved with inorganic materials can be fabricated with organic materials. Higher EO activity means that a lower power electrical signal can be used in the device, which reduces heat.

Organic EO materials can be used in many applications, such as improved EO modulator materials, light-harvesting and optical amplifier materials,

#### Impact

- EO material fabrication process provides lower device cost and allows conformal and flexible devices
- First demonstration of single-walled carbon nanotube actuators
- EO materials technology developed commercialized by Lumera
- Led to development of increased bandwidth systems crucial for telecommunications

electronic memory materials, LED materials, frequency converters, waveguides, and on-chip optical interconnects.

Advances made by the MURI team in the area of dendritic polymer materials were commercialized by a company called Lumera, based in Bothell, Washington. Lumera acquired the EO polymer intellectual property (IP) in 2000. In 2008, Lumera offered a 40-Gbps EO polymer modulator for optical-transmission systems. Devices with inorganic crystalline optics had consisted of only 10-Gb modulators and thus required four 10-Gbps modulators in series to achieve this level of performance.<sup>4</sup> Lumera also introduced a 100-Gbps modulator in November 2007. These modulators combined the fastest switching speeds with the lowest drive voltages (thus, low heat) and optical losses in the industry and also offered frequency ranges (35–140 GHz) not available with then-current crystalline materials.<sup>5</sup> This important capability provides systems increased bandwidth crucial for applications, such as telecommunications.

<sup>&</sup>lt;sup>3</sup> Mitch Jacoby, "High-Speed Organic Electro-Optics," *Chemical and Engineering News* 88, no. 51 (2010): 20.

<sup>&</sup>lt;sup>4</sup> See "Lumera Lights Up the Lines," <u>http://www.mdatechnology.net/update.aspx?id=a5341.</u>

<sup>&</sup>lt;sup>5</sup> Ibid.

The research from this MURI resulted in 9 patents and 29 derived patents. Also, the MURI team produced 138 publications that generated 4,203 citations. In addition, this MURI supported 10 graduate students and 12 post-doctoral fellows.

**Impact on DoD:** Dendrimer-based EO modulators exhibit operational bandwidths of several hundred gigahertz. Such modulators will be critical components of next-generation Internet communication, electronic countermeasures, mobile data management platforms, and radar systems. Indeed, Boeing and Motorola are proposing to develop data management components for the next-generation Airborne Warning and Control System (AWACS), using the materials and concepts developed in this MURI. Other applications include cable television (high-speed transmission of video data), high-speed switching nodes in fiber-optic communication networks, backplane interconnects for high-speed computers, ultrafast data processing (e.g., analog-to-digital conversion), remote voltage sensing, radio frequency (RF) distribution, optical gyroscopes, and improved land mine detection antenna systems.

## New Hybrid Route to Biomimetic Synthesis

In the 1960s, Otto Schmitt (1913–1998) coined the terms "biomimicry" and "biomimetics." Biomimicry, in its strictest sense, means "to imitate life," from the Greek bios or "life" and mimesis or "to imitate." Biomimetics, considered a relatively new science, focuses on studying nature, its models, elements, processes, and systems, which it then applies—either in the form of inspiration or direct imitation—to solve human and technological problems. This Multidisciplinary University Research Initiative (MURI) focused on biomimetic synthesis. The basic underlying premise is that analysis and creative adaptation of the mechanisms used to control mineral-organic composite synthesis in living

New Hybrid Route to Biomimetic Synthesis (1996–2002)

Professor Daniel E. Morse Department of Molecular, Cellular, and Developmental Biology University of California, Santa Barbara

> Sponsor: Army Research Office Dr. William Mullins

systems can lead to the development of novel routes to the synthesis of high-performance hybrid materials uniquely suited to advanced applications of interest to DoD.

**Objective:** The goal of this MURI was to develop economical low-temperature routes to the biomimetic synthesis of high-performance composite materials, with control of composition and structure based on the molecular mechanisms controlling biomineralization of calcium- and silicon-based nanocomposites. The anticipated advantages for materials synthesis included new insights into the mechanisms used by biology to control nanofabrication and hierarchical synthesis with structural precision exceeding the capabilities of present human engineering; more intimate coupling at the organic-inorganic interface in hybrid materials; and novel routes to synthesis and structural control of high-performance composites, over multiple, hierarchically controlled length scales under environmentally benign conditions.

Achievements: By focusing on a few carefully selected model systems of biomineralization involving silicon and calcium and using a highly integrated interdisciplinary approach that united the skills and approaches of researchers in six different departments and two universities, this research more than delivered on the originally proposed transition from analysis of biological systems to the development of useful processes across a broad range of materials. In particular, previously unanticipated mechanisms controlling the nanofabrication of mineralized

composites in living systems were discovered, and these basic insights were applied in the development of novel routes for the synthesis of high-performance mineral-organic composites, including oriented mesoporous and macroporous materials with a wide range of functionalities and unique properties and with



Source: Morse, D. E. 1999. "Silicon Biotechnology: Harnessing Biological Silica Production to Construct New Materials." *Trends in Biotechnology* 17 (6): 231.

Figure 1. Genetically controlled Nanoscale Architecture of the Silica Wall of the Marine Diatom *Paralia sulcata* (30 µm in Diameter)

structural control extending over nanoscale, mesoscale, and macroscale dimensions(see Figure 1). Advanced applications of several of the resulting new materials are currently under development.

**Long-Term Significance:** This MURI demonstrated that it is possible to use biotechnology to resolve the mechanisms used by nature to make high-performance composites and then successfully apply the information to develop new routes to the synthesis of novel composites

with exceptional control of composition and nanostructure. Highlights include the discovery that the silicateins—proteins that this team originally discovered were responsible for the structure-directing catalysis of polymerization to form silica and silsesquioxanes—can also be used for the structure-directing polymerization of titanium dioxide from the appropriate water-stable alkoxide precursor. This result dramatically extended the development of a new field called "Silicon Biotechnology" to an even broader "Functional Inorganic Materials Biotechnology." This MURI also demonstrated that the self-assembling diblock copolypeptides, which were developed as biomimetic analogs of the silicateins, can be used to direct the nanofabrication of potentially valuable core-shell fluorescent quantum dots and narrow linewidth micro-lasers. Finally, it discovered the mechanism of synthesis of the natural micro/laminate armor of the abalone shell and a new class of self-healing polymers that combine the strength of Kevlar with the toughness of silicones.

#### Impact

- Discovered that the silicateins can also be used for the structuredirecting polymerization of titanium dioxide
- Essentially started a new field of science and technology called "Functional Inorganic Materials Biotechnology"
- Used biomimetics to fabricate coreshell fluorescent quantum dots and narrow line-width microlasers
- Discovered the mechanism of synthesis of the natural micro/ laminate armor of the abalone shell
- Technology transferred to 12 companies

The research from this MURI produced 29 patent applications. Also, the MURI team produced 149 peer-reviewed publications and 244 conference presentations. This MURI supported a large team of developing scientists, which included 41 post-docs, 37 graduate students, and 29 undergraduate students. Many of these students moved on to jobs in leading industrial and government research labs and to positions in top universities across the nation.

**Impact on DoD:** This MURI developed processes for templated growth of materials with characteristics that are important to DoD (e.g., toughness). Based partly on the success of this MURI, the Army created a University Affiliated Research Center (UARC), with Dr. Morse as the founding director of the Institute for Collaborative Biotechnologies (ICB). In addition, based on this line of research, Dr. Morse was honored as one of the top 50 technology innovators of 2006 by *Scientific American* magazine for his development of bio-inspired, kinetically controlled routes to semiconductor thin films and nanoparticles.

This line of research has shown how biological systems accomplish precise synthesis of nanostructured materials and components with three-dimensional (3D) nanoscale architectural control. Through biomimetics, these processes can be duplicated, and the impact on U.S. military systems may be significant, with applications such as adaptive camouflage and improved armor. This MURI, with its focus on biomimetic synthesis, built a foundation for the subsequent work in this area.

## **Photonic Band Engineering**

Photonic crystals are artificially engineered, periodic structures designed to affect the motion of photons in the same way that the periodicity of a semiconductor crystal affects the motion of electrons. These structures allow unprecedented control of electromagnetic (EM) waves at radio, microwave, infrared (IR), or optical frequencies.

In 1987, two seminal papers on photonic crystals were published by Eli Yablonovitch<sup>1</sup> and Sajeev John.<sup>2</sup> Slowly, the number of research papers about photonic crystals began to grow. However, due to the difficulty Photonic Band Engineering (1996–2001)

Professor Eli Yablonovitch Department of Electrical Engineering University of California, Los Angeles

> Sponsor: Army Research Laboratory Dr. Henry O. Everitt

of fabricating these structures, early studies were either theoretical or in the microwave regime, where photonic crystals can be made more easily. In fact, in 1991, Yablonovitch demonstrated the first three-dimensional (3D) photonic bandgap in the microwave regime.<sup>3</sup> The structure involved an array of holes drilled in a transparent material, where the holes of each layer form an inverse diamond structure, known today as Yablonovite.

**Objective:** The goal of the Photonic Band Engineering Multidisciplinary University Research Initiative (MURI) was to determine novel capabilities based on the unusual photonic bandgap structure exhibited by photonic crystals, especially those that were fabricated using two-dimensional (2D) films.

Achievements: Scientists at the University of California, Los Angeles, the California Institute of

Technology, and the Polytechnic Institute of New York University achieved several important breakthroughs in various areas of photonic band engineering. Most importantly, they established the validity of using 2D thin film slab photonic crystals as a viable alternative to 3D structures, thereby greatly simplifying the technological demands of photonic crystals. These 2D structures opened up the possibility of creating photonic crystals using straightforward photolithography, which is very much in the mainstream of conventional technology. This discovery led to the commercialization of optical photonic crystal structures (see Figure 1) much faster than had been originally expected. Among the specific accomplishments in 2D photonic crystals are as follows: the smallest EM cavity every made, the smallest laser ever made, and the demonstration of spontaneous emission enhancement and suppression in 2D photonic crystals.



Figure 1. Optical Fibers Based on Photonic Crystals Can Be Used to Guide Light

Note for Figure 1: The cladding, which consists of several hundred capillary tubes, forms a photonic bandgap material that confines light to the central hole, which is about 15  $\mu$  in diameter (left). The pattern of colors illustrates how the confinement varies for different wavelengths (right).

<sup>&</sup>lt;sup>1</sup> Eli Yablonovitch, "Inhibited Spontaneous Emission in Solid-State Physics and Electronics," *Physical Review Letters* 58, no. 20 (1987): 2059–2062.

<sup>&</sup>lt;sup>2</sup> Sajeev John, "Strong Localization of Photons in Certain Disordered Dielectric Superlattices," *Physical Review Letters* 58, no. 23 (1987): 2486–2489.

<sup>&</sup>lt;sup>3</sup> E. Yablonovitch et al., "Photonic Band Structure: The Face-Centered-Cubic Case Employing Nonspherical Atoms," *Physical Review Letters* 67, no. 17 (1991): 2295–2298.

This MURI also showed that long-wavelength, lowfrequency photonic crystals are practical and can be quite compact—which is important for radio and microwave applications relevant to commercial and military systems. The key breakthrough was the development of a new type of photonic crystal, based on liquid crystal (LC) resonators, which can be much smaller than the EM wavelength. When the LC resonators are periodically distributed in space, interesting and compact EM bandgap structures result. In effect, the periodicity of such a photonic crystal is determined by the size of the LC resonators rather than by the EM wavelength, as had been previously thought. An example is a 2D array of LC resonators above a conventional metallic ground plane. This formation results in a

#### Impact

- Demonstrated validity of thin, two-dimensional photonic crystals for radio and microwave transmission
- Produced smallest EM cavity and laser
- Developed 3 start-up companies, and technology transferred to nine other companies and five federal laboratories

high impedance ground plane that has novel applications in the control of EM waves that can be useful for high precision Global Positioning System (GPS) antennas, efficient radio transmitters, and cellular telephones.

**Long-Term Significance:** The field of photonic crystals was aided at a critical point in its development by this MURI. As a result of the government's investment in this research, interest in photonic crystals and their applications exploded. For example, initially, the 1987 papers of Yablonovitch and John were not attracting very much attention. Since this MURI, however, Yablonovitch's paper alone has had over 7,600 citations, which is the second highest citation count of any paper published in *Physical Review Letters*. This MURI itself produced 160 publications.

An indication of the commercial interest in this research is the fact that this MURI spawned 5 patents, which, in turn, gave rise to an additional 100 derived patents. This MURI also resulted in three startup companies, and the technology was transferred to nine other companies and five federal laboratories.

This MURI supported 32 students, 23 post-docs, and 8 faculty at three leading universities in the United States. Many of the students went on to jobs in leading industrial and government research labs and to positions in top universities across the nation. Also, 14 PhDs and 7 Master's Degrees were awarded.

**Impact on DoD:** This single MURI spurred new technological advances that have had a tremendous effect on DoD. Nanophotonic waveguides are the ideal platform for creating mid-infrared devices such as optical parametric amplifiers. DoD has awarded many contracts for applications based on photonics components. Today, these components are incorporated into mid-infrared imaging technology for unmanned aerial vehicles (UAVs) and are being used in building electronic image intensifiers for the Army. Future DoD systems using electronic-photonic integrated circuits (EPICs) would not be possible without the key developments provided by this MURI. Henry Everitt, the program manager (PM) for this MURI commented that "By focusing on how precedent scientific breakthroughs can be developed and shepherded in directions of DoD relevance, MURIs have become an essential skunkworks for creating innovation for the warfighter."

## An Integrated Approach to Intelligent Systems

Computer-aided control of complex systems is becoming more important as unmanned and singleagent/multi-agent autonomous systems become more ubiquitous. This early project was truly revolutionary because it elucidated many of the principles for the control of these complex systems. It also developed the first embedded software that formed the basis for the computer-aided control of unmanned systems and provided the foundations for the development of fully autonomous systems that are now slowly being tested and fielded.

**Objective:** This Multidisciplinary University Research Initiative (MURI) focused on (1) developing the

embedded software for the control of single and multi-agent intelligent systems, (2) significantly advancing the state of the art in perception systems (e.g., computer vision) using a hierarchical aggregation of sensors, (3) developing a framework for representing and reasoning with uncertainty, and (4) advancing soft computing and the design of complex systems. See Figure 1.

Achievements: This MURI also provided the analytic tools and framework for the following:

- A theory of analysis, verification, and synthesis of control laws for hybrid systems;
- Software tools for simulation of hybrid multimodal systems (e.g., war games such as capture the flag with a mix of human and robotic players);
- The integration of multi-agent objectives into consistent, safe plans with performance metrics to quantify the emergent behavior (e.g., air traffic control (ATC) collision avoidance protocol);

An Integrated Approach to Intelligent Systems (1996–2001)

Professor Shankar Sastry Electronics Research Laboratory University of California, Berkeley

> Sponsor: Army Research Office Dr. Jagdish Chandra Dr. Linda Bushnell



Figure 1. Provably Safe Protocols for Aircraft Interaction

- A fundamental new theory for the integration of control and sensory hierarchies (especially visual) with application to automated driving and teleprescent environments;
- Novel methods for segmentation of images, implementation of low-level vision algorithms on neural network hardware, and the use of chaotic neural networks for representing complex patterns;
- Provably convergent algorithms for reinforcement learning; and
- Model-based approaches to soft computing involving fuzzy control and genetic algorithms.

**Long-Term Significance:** This MURI was truly foundational because it played a major role in establishing the field of hybrid control systems. The MURI team from the University of California, Berkeley (S. Shankar Sastry), Cornell University (Anil Nerode) and Stanford University (Zohar Manna) was instrumental in establishing a community working on the Computation and Control of Hybrid Systems. The team also organized the very first workshops in this field. These original workshops have evolved into two separate 1-week-long international conferences on Cyber Physical Systems and Embedded Systems that are now sponsored by the Association for Computer Machinery (ACM) and the Institute of Electrical and Electronics Engineers (IEEE), respectively. These conferences and their content can be traced directly to this seminal MURI project.

This MURI has made many fundamental contributions to the theory and algorithms for the control of intelligent systems. These contributions, which were outlined in the Achievement section, had significant implications for collision-avoidance systems, autopilot, and auto-lander systems and have evolved into the complex control systems for unmanned and autonomous vehicles. They also have implications for optimizing the strategy for war games such as capture the flag, in which the human interaction with autonomous and unmanned vehicles and computing and communication systems has to be coordinated and controlled (see Figure 2).

#### Impact

- Fundamental basis for hybrid control systems
- Control systems for Collision
  Avoidance Systems for ATC
- Theoretical foundation for control of unmanned and autonomous systems

The research from this MURI contributed over 200 papers to peer reviewed journals and conference proceedings. In addition, it supported 8 post-doctoral fellows and 2 undergraduate students and produced 13 PhDs.



Figure 2. Teaming Up Humans and Robots

**Impact on DoD**: This MURI provided some of the foundational control methods that set the stage for the rapid development and deployment of unmanned and autonomous systems for DoD. The Defense Advanced Research Projects Agency (DARPA) and the Service labs have had multiple subsequent research efforts in this domain.

Drones are now a key component of our military strategy, and their development was enabled by the seminal work done in this MURI. Key partners in the work were some of the major DoD contractors, including Boeing and Northrup Grumman in the area of unmanned aerial vehicles (UAVs), Honeywell Technology Center in the area of hybrid systems for flight management, and SRI in the area of verification tools. Future military systems will certainly include fully autonomous vehicles to support a small warfighter contingent and will be fully coordinated under intelligent control.

### Enhanced Electromagnetic and Chemical/Biological Sensing Properties of Atomic Cluster-Derived Materials

Nanotechnology is science, engineering, and technology performed at the nanoscale, or ~1–100 nm.<sup>1</sup> Under the direction of Dr. George C. Schatz, research at the Multidisciplinary University Research Initiative (MURI)-funded Center for Atomic Clusters-derived Materials at Northwestern University included the synthesis, characterization, and use of atomic and molecular clusters, nanoparticles, and nanomaterials.

The Center for Atomic Clusters-derived Materials performed a broad range of research. One of the most important results was the development of a nanoparticle-based technology for deoxyribonucleic acid (DNA) detection that has now been commercialized



and holds the promise of revolutionizing this field. A second important result was the development of a method for chemical and biological agent detection based on localized surface plasmon absorption.

**Objective:** The goal of this MURI was to focus on the emerging field of nanotechnology in relation to nanoparticles and explore diverse areas such as chemical and biological sensing, optical communications, molecular electronics, infrared (IR) detection, and advanced magnets.<sup>2</sup>

Research included varied projects, such as chemical and biological detection via localized surface plasmon absorption; structural characterization of atomic cluster Group 14 elements; carbon nanotube conductivity and mechanical properties; optical property theory, electronic conductivity theory, and the theory of DNA melting; new methods for metal nanoparticle synthesis and nanoparticles modified with organics and/or DNA; synthesis and characterization of new metal nanoparticles; and the first observation of non-linear optical properties of nanoparticles (e.g., hyper-Rayleigh scattering).<sup>3</sup>

Achievements: The most noteworthy development from this MURI was a colorimetric nanoparticle-based DNA (i.e., nucleic acid) detection technology. "[It] holds the promise of revolutionizing this field," Dr. Schatz states in the Final Progress Report,<sup>4</sup> a claim that holds true today. In 2012, the term Spherical Nucleic Acid (SNA) was coined to describe this novel nucleic acid architecture comprised of densely packed and highly oriented nucleic acids attached covalently to a nanoparticle surface.<sup>5</sup> The early stages of SNA research and its long-term significance are highlighted below.

DNA/gold particle biosensors are engineered by surface functionalizing an oligonucleotide (i.e., DNA) with an alkylthiol. The oligonuclueotide/alkylthiol constructs are then covalently attached to a gold nanoparticle<sup>6</sup> to create the DNA/gold particle biosensor (see Figure 1(a)). If the targeted DNA (referred to as a DNA linker) is present in a sample, it initiates hybridization and

<sup>&</sup>lt;sup>1</sup> See "What is Nanotechnology?," <u>http://www.nano.gov/nanotech-101/what/definition</u>.

<sup>&</sup>lt;sup>2</sup> George C. Schatz, Enhanced Electromagnetic and Chemical/Biological Sensing Properties of Atomic Cluster-Derived Materials, Final Progress Report for ARO Grant DAAG55-97-1-0133 (Research Triangle Park, NC: U.S. Army Research Office, 2003), 4.

<sup>&</sup>lt;sup>3</sup> Ibid., 1.

<sup>&</sup>lt;sup>4</sup> Ibid., 4.

<sup>&</sup>lt;sup>5</sup> Joshua I. Cutler et al., "Spherical Nucleic Acids," *Journal of the American Chemical Society* 134, no. 3 (2012): 1376–1391.

<sup>&</sup>lt;sup>6</sup> Chad A. Mirkin et al., "A DNA-Based Method for Rationally Assembling Nanoparticles into Macroscopic Materials," *Nature* 382 (15 August 1996): 607–609.

aggregation of the DNA/gold nanoparticle biosensors creating a noticeable color change (purple) that can be detected via absorption or scattering (see Figure 1(b)). Electrical conductivity can also be detected.<sup>7</sup>



Source: Mirkin, Chad A. 2011. "MURI-Funded Scientific and Technological Blockbusters from Northwestern University." Evanston, IL: Department of Chemistry and the International Institute for Nanotechnology. <u>http://www.dtic.mil/ndia/2011disruptive/Mirkin.pdf</u>.

Figure 1. Hybridized Aggregates of DNA/Gold Nanoparticles Show Distinct Color Changes in Their Hybridized (Purple) and Unhybridized (Red) Forms

The Center for Atomic Clusters-derived Materials was funded at a crucial point in the development of these SNAs. In 2000, Dr. Chad Mirkin, a co-principal investigator (PI), formed the

startup company Nanosphere, Inc., to market this highly selective and sensitive nucleic acid detection technology. Its capability as a biological detection technology was demonstrated for anthrax, tularensis, and other pathogens and included field tests at Dugway Air Force Base in Utah.<sup>8</sup>

**Long-Term Significance**: SNAs have been studied extensively, and their applications have been expanded to include medical diagnostics and therapeutics that can be used to treat a variety of genetically based ailments. Another important property of these DNA/gold nanoparticle aggregates is their surprisingly narrow melting transitions when compared to the same unmodified DNA.<sup>9</sup> This fundamental difference has been the basis for using these nanoparticles as

#### Impact

- Development of a colorimetric nanoparticle-based DNA detection technology
- Start-up Nanosphere, Inc. that produced the Verigene system, with the FDA
- One of the key developments that led to the establishment of the National Nanotechnology Initiative by President Clinton

probes for medical diagnostic tools. The most successful commercial innovation has been Nanosphere's Verigene system, with Food and Drug Administration (FDA)-cleared tests for respiratory viruses, blood cultures, warfarin metabolism, and others. It is presently used in hospitals and clinical settings globally.<sup>10</sup>

Shortly before the start of this MURI in 1996, Dr. Chad Mirkin, a co-PI at Northwestern University, published a groundbreaking paper on DNA-modified gold nanoparticles—a DNA-based method for rationally assembling nanoparticles into macroscopic materials. A publication during this MURI in 1997 showed the suitability of these DNA-modified gold nanoparticles as biological sensors. These two pivotal papers are listed on the Mirkin Research Group's website as his

<sup>&</sup>lt;sup>7</sup> So-Jung Park, et al., "Array-Based Electrical Detection of DNA with Nanoparticle Probes," *Science* 295, no. 5559 (22 February 2002): 1503–1506.

<sup>&</sup>lt;sup>8</sup> George C. Schatz, Enhanced Electromagnetic and Chemical/Biological Sensing Properties of Atomic Cluster-Derived Materials, Final Progress Report for ARO Grant DAAG55-97-1-0133 (Research Triangle Park, NC: U.S. Army Research Office, 2003), 5.

<sup>&</sup>lt;sup>9</sup> Ibid., 9.

<sup>&</sup>lt;sup>10</sup> See "Nanosphere," <u>http://www.nanosphere.us/page/about-us</u>.

two most cited scientific papers—with over 4,900 citations—and have been credited with the launch of his very prolific scientific career. Of the 28 papers that Mirkin attributes to this MURI, 5 are included in his website's list of his 10 most cited papers. The co-PIs at Northwestern University and Georgia Tech, along with collaborators at Chicago State University, Lucent, and the Naval Research Laboratory (NRL), published 113 peer-reviewed papers during this MURI.

One Mirkin patent<sup>11</sup> and two derived patents are credited to this MURI. However, these numbers grossly underestimate the commercial interest and long-term significance of this technology. Nanosphere's patent portfolio has expanded to include 151 issued patents and 52 pending patents.<sup>12</sup> Although it is difficult to discern which of these patents are derived from this MURI, the company's commercial success is a testament to this MURI's impact. One further testament to the significance of this pioneering effort is that Chad Mirkin is the first double recipient of the prestigious DoD-sponsored National Security Science and Engineering Faculty Fellow (NSSEFF) Award.

**Impact on DoD**: Chemical and biological threats are changing rapidly. The advancement and global proliferation of these threats greatly extends the spectrum of possible actors, agents, concepts of use, and targets. DoD must therefore continuously develop new defensive capabilities to stay ahead of a rapidly evolving threat. Biological threats are considered "weapons of mass destruction," and DoD has significant countermeasure projects that have their basis in technology that was pioneered in this MURI. Therefore, the impact of this MURI, with its demonstrated capability to detect anthrax, tularensis, and many other pathogens, is very significant to DoD.

<sup>&</sup>lt;sup>11</sup> Chad A. Mirkin and Sonbinh T. Nguyen, Nanoparticles with polymer shells, U.S. Patent 7115688, filed November 30, 1999, and issued October 3, 2006.

<sup>&</sup>lt;sup>12</sup> See "Nanosphere: Global Technology Patent Portfolio," <u>http://www.nanosphere.us/page/about-us</u>.

## The Design and Control of Smart Structures

Smart structures can be thought of as solutions to technological problems that use the controllability of physical effects such as magnetostriction, electrostriction, piezoelectric effects, and electroosmosis to achieve their function. This emerging area of engineering was made possible by developments in material science, micro-fabrication, and the availability of analog and digital electronics capable of generating the precise, high-frequency waveforms necessary to take advantage of such effects.

**Objective:** The objective of this Multidisciplinary University Research Initiative (MURI) was to advance the state of the art in the active control of The Design and Control of Smart Structures (1997–2003)

Professor Roger W. Brockett Department of Computer Science and Electrical Engineering Harvard University

> Sponsor: Army Research Office Dr. Randy Zachery

materials and structures. It explored five important areas related to smart materials and structures: (1) microfluidics, (2) micromagnetics, (3) adaptive optics, (4) microelectromechanical systems (MEMS) fabrication, and (5) control architectures. The emphasis ranged from addressing fundamental questions on modeling of magnetic materials to developing new techniques in the control of fluids and fabricating novel devices based on these techniques. See Figure 1.

Achievements: Scientists from Boston University, Harvard University, and the University of Maryland achieved several important breakthroughs during this MURI. For example, in the field of microfluidics, work on the control of boundary layer flow and the position of fluid interfaces led to the development of an optical switch capable of switching a light beam at up to 1,000 Hz using the electrostatic deflection of a conductive/dielectric fluid interface approximately

.025 inches in diameter and .01 inches deep. Optimal control principles played an important role in improving the switching speed. In the area of control architectures, this MURI established the first statement of what has become known as the data-rate theorem, which places bounds on the minimum data rate required to stabilize a system.

Long-Term Significance: Significant progress has been made in the design of MEMS mirrors and MEMS arrays of silicon-based micro-valves and in the design and fabrication of arrays of silicon-based MEMS piston actuators for applications in adaptive optics. This MURI capitalized on a proven and highly successful collaboration between



Source: Perreault, Julie A. et al. 2002. "Adaptive Optic Correction Using Microelectromechanical Deformable Mirrors," *Optical Engineering* 41 (3): 561

## Figure 1. Elements of a Simple Adaptive-Optical Imaging System

researchers at the Boston University Photonics Center and researchers at the Army Research Laboratory (ARL). Prototype micro-mirror arrays fabricated at the Photonics Center were incorporated into test beds for laser communication and/or adaptive wavefront control at the ARL, Lawrence Livermore National Laboratory (LLNL), Lockheed Martin Missile Systems, the National Aeronautics and Space Administration's (NASA) Jet Propulsion Laboratory (JPL), the University of Victoria, the Imperial College London, the Rochester Visual Sciences Center, the Schepens Eye Research Institute, and the Adaptive Optics Associates Corporation. This project resulted in four important milestones:

- The fastest adaptive optics control loop ever demonstrated (11 kHz),
- The first real-time adaptive optical imaging system to improve resolution using MEMS,
- The first demonstration of a laser-communication link using real-time adaptive compensation and a MEMS mirror, and
- A comprehensive analysis of the opto-electro-mechanical performance of MEMS devices in adaptive control systems.

Another project involved an optical system consisting of a 324-element silicon spatial light modulator embedded into an optical free-space laser communication link to allow high-speed control of the wavefront phase. This system is being used in research concerning compensation of path aberrations and enhancement of security in point-to-point data links. Much of the micro-mirror technology developed during this project was licensed by Boston University for production by Boston Micromachines Corporation (BMC). Commercial sales of this pilot product in the first 2 years exceeded \$400,000. In addition, in a subsequent collaboration supported by DARPA, the Boston University/BMC team fabricated a device with 1,024 pixels and improved optical quality.

Impact

- Developed the fastest adaptive optics control loop ever demonstrated
- Demonstrated first lasercommunication link using realtime adaptive compensation and a MEMS mirror
- Demonstrated a novel optical switch based on the control of a fluid/fluid interface
- Technology transferred to four companies

This MURI supported more than 60 students at the under-

graduate, graduate, and post-doctoral levels, many of whom moved on to jobs in leading industrial and government research labs and to positions in top universities across the nation. In addition, the research from this MURI produced 160 papers, which have generated over 1,400 citations.

**Impact on DoD:** The importance of this MURI to a wide range of U.S. military systems is clear. High-resolution laser-wavefront modulation addresses a critical military need. The military impact of this MURI research is measurable in terms of superior targeting capability for laserguided ordinance and improved stealth in point-to-point optical communications. The significance of this MURI to DoD will continue to increase as this technology begins to be fielded in numerous U.S. military systems.
## Adaptive Optoelectronic Eye

Adaptive optoelectronics is an important technology for optical sensing and imaging. It is based on components whose properties can be modified adaptively in real time so that, for example, the focal point of an imaging array can be changed as the object to be imaged moves.

**Objective:** The goal of this Multidisciplinary University Research Initiative (MURI) was to develop a versatile image sensor technology that would mimic the functions of the human eye—a technology that merged advances in optoelectronics with adaptive micro-optics and micromechanical subsystems.

Adaptive Optoelectronic Eye (1998–2003)

Professor Pallab Bhattacharya Department of Electrical Engineering and Computer Science University of Michigan

> Sponsor: Army Research Office Dr. Michael Gerhold

Achievements: This MURI demonstrated several key components of an artificial eye, including a variable focus Fresnel lens incorporating multiple quantum wells (MQWs) and a micromachined platform for steering the optical elements. A schematic of an artificial vision system incorporating these components is illustrated in Figure 1. Other key components developed by this MURI that have had an important and lasting impact on the field of optoelectronics were the



Source: Bhattacharya, Pallab. 2003. *Adaptive Electronic Eye*. Final Report: June 1, 1998–November 30, 2003. Ann Arbor, MI: University of Michigan, 7.

#### Figure 1. Schematic of an Artificial Vision System Incorporating a MQW Fresnel Lens and a Bio-Photoreceiver Array

development of a new class of solid-state lasers and light-emitting diodes (LEDs) based on microcavities with embedded quantum wells and quantum dots. These high-performance devices are the basis of current photo transceivers that are used pervasively in our optical communication networks. In fact, the incorporation of quantum dots in the laser microcavity was a crucial development that lowered the threshold and also raised the efficiency and gain of these solid-state lasers and concomitantly LEDs.

**Long-Term Significance:** The essential components of the adaptive optoelectronic eye are the front-end optical system, the

detector array, and the back-end processing. A significant achievement of this MURI was the development of a Fresnel lens-modulator using an MQW. This lens demonstrated bias-dependent dual-focus behavior and a 7:1 ratio in focused intensity modulation. Further analysis showed that this focusing effect was mainly due to the absorption change caused by the quantum-confined Stark effect (QCSE) rather than the modification of refractive index. Variable focus was achieved by stacking two MQW Fresnel lenses together. Although the demonstration reported during the MURI effort was with near-infrared (IR) excitation, the lens can, in principle, be designed for visible illumination, using wide-bandgap heterostructures.

A co-principal investigator (PI) on this MURI, Professor Dennis Deppe (University of Texas at Austin), was one of the major inventors of quantum dot lasers. Although some of his seminal work predated this project, he continued to refine and improve these devices as a result of this MURI. Also, as part of this MURI, he developed the  $1.5-\mu$  wavelength devices that are so important for optical communications. Diana Huffaker, one of Professor Deppe's post-docs

during this MURI and the first author on many of the key papers on quantum dot lasers, is now a Professor at the University of California at Los Angeles and a National Security Science and Engineering Faculty Fellow (NSSEFF) and continues to work on optoelectronics.

This MURI also had a profound effect on the career of Professor Bhattacharya, who is now a member of the National Academy of Engineering and the recipient of several major awards. The research from this MURI produced 19 peerreviewed journal articles, 9 conference presentations, and 22 invited or plenary talks. It also supported 7 postdoctoral fellows, and 23 graduate students. In addition, one

#### Impact

- Development of a dual-focus • Fresnel lens and micro-machined platform for steering optical elements
- Designed, fabricated, and • demonstrated novel microcavity LEDs with quantum well and quantum dot active regions

patent disclosure was based on the research conducted in this MURI.

**Impact on DoD:** The development of an agile sensor technology able to detect, process, and transmit near-perfect optical images and related information that would adapt automatically to changing scenarios and environments is essential to DoD's intelligence, surveillance, and reconnaissance (ISR) mission. By merging microelectronics, micro-optics and micromechanical components with advances in optical devices, this MURI demonstrated the feasibility of such a versatile image sensor technology, such as the Defense Advanced Research Projects Agency (DARPA) project on the Adaptive Focal Plane Array.

## Compact Power Supplies Based on Heterojunction Switching in Wide-Bandgap Semiconductors

The recent emergence of wide-bandgap semiconductors, such as silicon carbide (SiC) and gallium nitride (GaN), promises new devices that are likely to revolutionize areas as diverse as high-speed communications, advanced radar, integrated sensors, solar-blind ultraviolet (UV) detectors, high-temperature electronics, and power control and switching. The materials properties of both of these semiconductor systems make them well suited for operation at higher temperatures and frequencies and at electrical current or voltage levels inaccessible to standard silicon-based electronics. That said, in the late 1990s significant challenges remained, including film quality and device performance.

Compact Power Supplies Based on Heterojunction Switching in Wide-Bandgap Semiconductors (1998–2004)

Professor Robert F. Davis Department of Materials Science and Engineering North Carolina State University

> Sponsor: Office of Naval Research Dr. Harry Dietrich

**Objective:** The goal of this Multidisciplinary University Research Initiative (MURI) was to address the significant materials and device challenges facing the use of wide-bandgap semiconductors in military systems. This MURI explored four important areas related to wide-bandgap semiconducting materials and devices: (1) theoretical and experimental investigations of carrier dynamics under very high electric fields; (2) epitaxial growth of low-defect density films of GaN and aluminum gallium nitride (AlGaN) on SiC substrates; (3) wafer bonding; and (4) design and fabrication of heterostructure devices based on wide-bandgap semiconductors for power switches and high-frequency power devices. The emphasis was on device advancements that enable significant improvements in broadband performance, high linearity, and/or high power added efficiency.

Achievements: Scientists at North Carolina State University, the University of California, Santa Barbara, and Rensselaer Polytechnic Institute achieved several important breakthroughs during this MURI. These achievements fall into three general categories:

- Crystal growth,
- Device processing and fabrication, and
- Theoretical work in carrier transport and device physics.

A notable achievement was the development of pseudo-epitaxy to grow GaN and AlGaN thin films with significantly lower defect densities. This process, illustrated in Figure 1, is an overgrowth technique in which stripes and/or other "seed" forms are etched through the nitride material and into the substrate. In so-called maskless pseudo-epitaxy, GaN or AlGaN is again grown laterally and vertically from the stripe material. The result is a film with a defect density five orders of magnitude lower than that achieved with traditional epitaxial techniques.<sup>1</sup> This capability has significant implications for device performance.



Source: Roskowski A. M. et al. 2002. "Reduction in Dislocation Density and Strain in GaN Thin Films Grown via Maskless Pendeo-Epitaxy." *Opto-Electronics Review* 10 (4): 262.

Figure 1. Schematic of Pseudo-Epitaxial Growth from a GaN Seed Laterally Off the Sidewalls and Vertically Off the Stripe

<sup>&</sup>lt;sup>1</sup> A. M. Roskowski et al., "Reduction in Dislocation Density and Strain in GaN Thin Films Grown via Maskless Pendeo-Epitaxy," *Opto-Electronics Review* 10, no. 4 (2002): 261–270.

Another important achievement in this MURI was the development of an insulated-gate AlGaN/GaN high-electron mobility transistor (HEMT) grown on a highly resistive GaN buffer layer. This device, illustrated in Figure 2, exhibited a breakdown voltage of 1.3 kV and a low specific onresistance of 1.65 m $\Omega$  cm<sup>2</sup>. A state-of-the-art power device figure of merit of V<sub>BR</sub><sup>2</sup>/R<sub>on</sub> = 9.94 × 10<sup>8</sup> [V<sup>2</sup>  $\Omega$ <sup>-1</sup> cm<sup>-2</sup>] was achieved.<sup>2</sup>

**Long-Term Significance:** The significance of this MURI is best illustrated by the speed with which the technology was transferred to industry. For example,

- The pseudo-epitaxy developments were licensed to the Nitronex Corporation.
- The Schottky barrier contact technology for p-type GaN was licensed to Cree, Inc.
- The AIGaN/GaN heterostructure bipolar transistor (HBT) technology was transferred to Hughes Research, Inc.
- The AlGaN/GaN HEMT technology was also transferred to Hughes Research, Inc.

The research from this MURI produced 14 patents and 9 non-patented invention disclosures. It also produced 235 peer-reviewed publications, 60 invited presentations, and 99 contributed presentations. It also supported 10 faculty, 6 post-doctoral fellows, 31 PhD students, and 3 Master's students. Many of the students went on to jobs in leading industrial and government research labs and to positions in top universities across the nation.

**Impact on DoD:** The importance of this MURI to a wide range of U.S. military systems is clear. The general goal of



Source: N.-Q. Zhang et al. 2001. "Effects of Surface Traps on Breakdown Voltage and Switching Speed of GaN Power Switching HEMTs" (Washington, DC: The International Electron Devices Meeting Technical Digest), 25.5.2.

#### Figure 2. Insulated Gate AIGaN/GaN HEMT

#### *Impact*

- Development of pseudoepitaxy for thin film growth
- Development of new contact technology for p-type GaN
- Demonstration of first AIGaN/GaN HBTs
- Development of insulatedgate AlGaN/GaN HEMTs
- Technology transferred to four companies

the program was the development of wide-bandgap semiconductor, low-noise, high-speed, and high-power devices and circuits for applications such as surveillance, electronic warfare, multifunctional radio frequency (RF) systems, communications, and power applications. Among other things, the program developed microwave switches for RF transmit/receive modules, X-band microwave power devices for phased array radar, low-noise amplifiers and wireless base stations for use in communications, and high-voltage switches for power control applications. The significance of this MURI to DoD will continue to increase as this technology begins to be fielded in numerous U.S. military systems.

<sup>&</sup>lt;sup>2</sup> N.-Q. Zhang et al., "Effects of Surface Traps on Breakdown Voltage and Switching Speed of GaN Power Switching HEMTs" (Washington, DC: The International Electron Devices Meeting Technical Digest, 2001), 25.5.1–25.5-4.

## Nanoshell-Based Infrared (IR) and Terahertz Adaptive Materials

Metallic-shelled nanoparticles that strongly interact with light were pioneered by Dr. Naomi Halas's group at Rice University starting in the late 1990s. The optical properties of these nanoparticle structures, which typically consist of a silica (dielectric) core surrounded by a thin shell of gold, can be tailored by controlling the size of the core and the thickness of the gold coating. Thus, the plasma frequency of these nanoparticles can be tuned from the visible spectrum through the terahertz region of the spectrum by changing the particle size from less than a micron to more than 10  $\mu$ . These structures exhibit a strong

Nanoshell-Based Infrared (IR) and Terahertz Adaptive Materials (1999–2005)

Professor Naomi Halas Electrical and Computer Engineering Rice University

> Sponsor: Army Research Office Dr. Marc Ulrich

absorption of optical energy at the plasma frequency, where the light is converted to electronic excitations called plasmons. These nanoparticles can be produced chemically "in a beaker" and by a nanoprint technique on a two-dimensional (2D) surface.

**Objective:** The goal of this Multidisciplinary University Research Initiative (MURI) was (1) the design and fabrication of nanoshell particles and closely related nanoparticle assemblies with tailored optical and electromagnetic (EM)responses over a wide spectrum of optical, IR, and terahertz wavelengths and (2) the development of breakthrough science and technology (S&T) that would enable the control and manipulation of EM radiation with unprecedented precision, based on components that can be produced in large quantities and at moderate costs.

Achievements: A key achievement that enabled much of what was to follow was the development of a theory for the plasmon response in finite metallic nanostructures of complex geometries such as the nanoshell (see Figure 1). This response is quite complicated, and this strong theoretical development enabled the Rice and Oklahoma State MURI team to design, fabricate, and test against the model the various nanostructures that they fabricated.

In characterizing the optical response of these nanoshells, the MURI team observed that the geometry of the structures could be modified through their thermal response and, even more importantly, that the properties of the surrounding materials could be modified significantly.



Source: Figure available at <u>http://pubs.acs.org/doi/abs/10.1021/nl060209w</u>. See also Wang, Hui et al. 2006. "Nanorice: A Hybrid Plasmonic Nanostructure." *Nano Letters* 6 (4): 827–832.

Figure 1. An Example of a Nanoshell Structure Called "Nanorice," Whose Properties Have Highly Tunable Plasmon Resonances Off the Stripe

These photo-thermal properties are key to the commercialization of these remarkable materials since they have been demonstrated to be capable of providing various opto-mechanical responses that have been extremely important in several key areas, including cancer therapy. It has been clearly demonstrated that passivated nanoshells of a certain geometry can be harmlessly injected into the body, where they naturally migrate to tumors. When the area closest to the tumor is subjected to IR radiation (that penetrates deep inside the body), the nanoshells absorb the radiation, heat up, and destroy the surrounding tumor. The Rice team has founded a company to commercialize this technology, which is currently in clinical trials.

This dramatic photo-thermal response has now been used for solar energy conversion that can turn water directly into steam. These nanoshells can be tailored to have their absorption band

match solar radiation; thus, just by suspending them in water and exposing the water to sunlight, the water turns almost instantly into steam. The conversion efficiency is approaching that of more conventional solar cells.

**Long-Term Significance:** The fundamental research conducted for this MURI has led to the development of nanoparticles that can be used to conceal Soldiers by scattering EM waves in the visible light and IR regions.

The MURI funding came soon after the group's original pioneering work was published.<sup>1</sup> This paper was the very first publication on metallic nanoshell structures and has been cited over 1,100 times. A seminal result that now underpins the field was subsequently developed in this MURI.<sup>2</sup> This

#### Impact

- Fabrication of nanoshell particles with a tailored optical/EM responses
- Development of thin-film
  structures with passive and
  active control of
  electromagnetic properties
- Development of nanoshellbased all-optical biosensor
- One start-up company

paper, which has been cited over 1,000 times, kick-started the field of nanoshell-based plasmonics and inspired the development of a major direction for this field: the imaging and treatment of cancer as presented in a highly cited paper.<sup>3</sup>

The research from this MURI produced four patents and eight derived patents. It also produced 89 peer-reviewed publications and 122 conference presentations, which generated over 1,500 citations. This MURI project supported 6 faculty and 27 graduate students.

**Impact on DoD:** The impact of this MURI is broad and potentially significant. Although plasmonics is relatively new, in the 10 years since this MURI, the field has gained significant momentum and is now enabling fundamental science and important new applications. Because plasmonics exploits the unique properties of metallic nanostructures to manipulate light actively at the nanoscale, it opens the possibility of ultra-high resolution imaging and control of optical processes with unprecedented precision. Moreover, because of its compatibility with traditional electronics, the circuits and systems composed of plasmonic and electronic devices hold promise for new generations of high-speed, broad-bandwidth, and low-power computing and communications.

<sup>&</sup>lt;sup>1</sup> S. J. Oldenburg et al., "Nanoengineering of Optical Resonances," *Chemical Physics Letters* 288, nos. 2–4 (1998): 243–247.

<sup>&</sup>lt;sup>2</sup> E. Prodan et al., "A Hybridization Model for the Plasmon Response of Complex Nanostructures," *Science* 302, no. 5644 (17 October 2003): 419–422.

<sup>&</sup>lt;sup>3</sup> Christopher Loo et al., "Nanoshell-Enabled Photonics-Based Imaging and Therapy of Cancer," *Technology in Cancer Research and Treatment* 3, no. 1 (2004): 33–40.

## **Semiconductor Radiation Physics: From Defects to Devices**

State-of-the-art electronics have to work reliably in all sorts of environments, including the very extreme ones encountered by many defense and space systems. In particular, the effects of radiation on these systems in some harsh environments need to be understood in great detail so that these effects can be mitigated by design and hardening fabrication techniques. Despite some successes in building radiation-hardened systems, many of the fundamental physics-based mechanisms responsible for radiation-induced degradation were not understood before this MURI was initiated. This lack of understanding made it difficult to extend any successes to future generations of devices based on new

Semiconductor Radiation Physics: From Defects to Devices 2000–2005

Professor Ronald Schrimpf Electrical Engineering and Computer Science Department Vanderbilt University

Sponsor: Air Force Office of Scientific Research Dr. Gerald Witt

materials or new principles of operation. This Multidisciplinary University Research Initiative (MURI) combined newly developed atomic-scale computational techniques and physical analysis tools to analyze and understand the effects of radiation on emerging semiconducting materials and electronic devices so that eventually the systems can be built appropriately. The team consisted of Vanderbilt University as the lead organization, North Carolina State University, the University of California, Berkeley, and the University of Arizona.

**Objective:** The objective of this MURI project was to study the effects of radiation on siliconbased microelectronics and compound semiconductor-based optoelectronics. In particular, this MURI focused on (1) studying the electronic and atomic dynamics resulting from exposure of materials and devices to a radiation environment, with the goal of understanding defect nucleation, evolution, and growth on the atomic scale; (2) understanding the relationship between the radiation-induced defect interactions to overall device performance in the radiation environment,



Figure 1. Hierarchical Multi-Scale Analysis of Radiation Effects

and (3) developing and validating engineering models suitable for incorporating into commercial Technology Computer-Aided Design (TCAD) tools for designing radiation-hard circuits and systems. This approach is illustrated in Figure 1, showing schematically the hierarchical development of device models and simulations from radiation effect experiments data.

Achievements: This MURI provided a fundamental foundation for understanding radiation effects in

semiconductors. Before this MURI was funded, according to Jerry

Witt, the Air Force Program Manager (PM), there was very little fundamental understanding of radiation effects on electronics because the academic community was not engaged in research in this area. This MURI resulted in the first effort to fully understand radiation effects in conventional silicon electronics, and just as importantly in emerging materials such as gallium nitride (GaN) and high-k gate dielectrics that have now become very important for DoD systems. Devices based on these latter materials were not in use when this MURI started, but they are now mainstream technologies.

**Long-Term Significance**: Four years after the start of this MURI and after the project was demonstrating success in elucidating the fundamental science of radiation effects in semiconductor electronics, the Vanderbilt team founded the Institute for Space and Defense Electronics (ISDE) (see Figure 2). The mission of ISDE is to take the results of the basic radiation effects research and apply it to DoD systems. Following the success of this MURI, an additional MURI was sponsored by the Air Force Office of Scientific Research (AFOSR), *Radia*-

Impact

- Instigated founding of ISDE
- Stimulated follow on MURI
- Go to organization for radiation effects on state-ofthe-art electronics

*tion Effects on Emerging Electronic Materials and Devices* (2005–2010), which continued the excellent work on the newest emerging materials and devices.



Source: http://www.isde.vanderbilt.edu/.



This MURI supported 10 professors, 7 research associates, and 14 students. One patent was filed, and 74 publications resulted from this project.

**Impact on DoD**: This MURI provided important information to DoD on the capabilities of electronics in equipment that is subject to high levels of radiation exposure. This information is important to electronics in our nuclear weapons, near nuclear power sources, and in satellites and space-based platforms. ISDE was founded as a direct result of this MURI and works closely with the Air Force Research Laboratory (AFRL), the Defense Threat Reduction Agency (DTRA), and all of the major defense and space corporations to provide the radiation effects models, tools, and testing capability to help design and validate their systems. These systems are important not only for our satellites and other space-based assets, but also for our strategic systems. For example, the work spawned by this MURI is a key component of the Navy Trident Life Extension Program. Vanderbilt's role was to develop the radiation effect models and tools for use in the Trident Missile guidance system. These models were based on mechanisms identified as part of the MURI program, particularly related to charge trapping and defect formation in insulators and interfaces.

## **Strategic Applications of Ultracold Atoms**

Many ultracold atoms exhibit measurable quantum behavior that can be exploited to create advanced matter wave sensors. These sensors have the potential for unprecedented levels of precision and accuracy. Sensors being investigated include gyroscopes, magnetometers, gravimeters, and gravity gradiometers. These sensors allow for extremely precise navigation systems as an alternative to satellite-based Global Positioning System (GPS) that could be compromised in military operations.

Strategic Applications of Ultracold Atoms (2000–2006)

Professor Mark Kasevich Physics Department Stanford University

Sponsor: Army Research Laboratory Dr. Peter Reynolds

**Objective:** The concept that atoms could collapse into the same quantum state was proposed by Satyendra

Nath Bose and Albert Einstein in a series of papers in 1924–1925.<sup>1</sup> The first Bose-Einstein Condensate (BEC) was achieved 70 years later. In 2001, Eric A. Cornell, Wolfgang Ketterle, and Carl E. Wieman were awarded the Nobel Prize "for the achievement of Bose-Einstein condensation in dilute gases of alkali atoms and for early fundamental studies of the properties of the condensates."<sup>2</sup> Since then, many groups have reproduced and expanded their work, turning BEC from a laboratory demonstration into a tool for studying basic physics properties. The goal of this Multidisciplinary University Research Initiative (MURI) was to use BEC to create advanced matter wave sensors that exceed the previous limits of previous generations of sensors by over two orders of magnitude.

Achievements: Scientists at the Massachusetts Institute of Technology (MIT), Harvard, Yale, Stanford, and the University of Arizona achieved several important breakthroughs during this MURI. Among the specific accomplishments were the following:

- Demonstration of atomic interferometry. A BEC was created and split into two parts. The phase of each condensate was allowed to evolve independently, and then they were recombined. The resulting matter waves created an interference pattern (see Figure 1).
- The coldest BEC made to date (500 picokelvin).
- Creation and study of BEC using molecules rather than atoms.
- BEC splitting and interference on an atom chip.
- Demonstration of BEC coherence in a waveguide.

This MURI showed that BEC can be used as the active component of a sensor in a compact device. In particular, the MURI team has demonstrated BEC formation in a magnetic microtrap on a silicon substrate. To fabricate a device that can be fielded, the size, weight, power, and cooling of the instrument must be reduced to a manageable amount. The team also demonstrated a novel miniaturized trap for lithium ions, which may be a better option than the more typical rubidium or sodium ions.

**Long-Term Significance:** This MURI boosted the development of the field of matter wave sensing at a critical point in its development. As a result of the government's timely investment, ultracold atomic and molecular condensates are no longer viewed as laboratory curiosities but rather as central components of devices for making extremely precise and accurate measurements.

<sup>&</sup>lt;sup>1</sup> S. N. Bose, "Plancks Gesetz und Lichtquantenhypothese" ("Plancks Law and Light Quantum Hypothesis"), *Zeitschrift für Physik* 26, no. 1 (1924): 178–181; A. Einstein, "Quantentheorie des einatomigen idealen Gases" ("Quantum Theory of the Monatomic Ideal Gas"), *Sitzungsberichte der Preußischen Akademie der Wissenschaften*, Vol. Physikalisch-mathematische Klasse (1924): 261–267.

<sup>&</sup>lt;sup>2</sup> See "Press Release: The 2001 Nobel Prize in Physics," http://www.nobelprize.org/nobel\_prizes/physics/laureates/2001/press.html.



Source: Ketterle, Wolfgang. 2004. Strategic Applications of Ultracold Atoms: MURI Fellowship for J. R. Abo-Shaeer. Cambridge, MA: Massachusetts Institute of Technology, Research Laboratory of Electronics, 4.

#### Figure 1. Matter Wave Interference

Note for Figure 1: (a) Absorption image of condensates released from the optical double-well potential and allowed to expand for 30 ms. The field of view is  $600 \ \mu m \times 350 \ \mu m$ . (b) Radial density profiles were obtained by integrating the absorption signal between the dashed lines, and typical interference patterns had greater than 60% contrast. The spatial phase of the matter wave interference pattern was extracted from the fit shown.

Commercial development of matter wave sensors is proceeding slowly. This MURI led to the development of one startup company, AOSense, which has contracts with the National Aeronautics and Space Administration (NASA) and the Defense Advanced Research Projects Agency (DARPA), among others, to develop quantum metrology devices, especially for precision navigation and timing.

This MURI project supported 9 faculty, 6 post-docs, and 22 students. Many of these students went on to jobs in leading industrial and government research labs and to positions in top universities across the nation. The research from this MURI also produced 61 journal articles and 74 conference papers.

Impact on DoD: For DoD, this MURI was highly successful in many ways. It energized research efforts to build extremely

#### Impact

- First demonstration of atomic interferometry in a Bose-Einstein Condensate (BEC)
- First BEC on a silicon chip and in a waveguide
- Formed a start-up, AOSense, which builds extremely precise navigation and timing devices

sensitive sensors using atom interferometry in general and Bose-Einstein condensed atoms specifically. These advancements led to precise navigation systems that would still be effective if GPS was compromised. In addition, these advances may lead to new capabilities in mapping underground spaces, which could impair an enemy's ability to hide weapons and facilities from view in deeply buried bunkers. Recently, researchers have calculated that a gravitometer employing gravity quantum interference could be used for detecting stealth aircraft, unmanned aerial vehicles (UAVs), and cruise and ballistic missiles.

Emmanuel David Tannenbaum, "Gravimetric Radar: Gravity-Based Detection of a Point-Mass Moving in a Static Background," arXiv:1208.2377 [physics.ins-det].

## Surface-Templated Bio-Inspired Synthesis and Fabrication of Functional Materials

A desirable trait in molecule-based materials is selfassembly, where the molecule itself is programmed through its chemical makeup to adopt a desired structure. Self-assembly allows precise control and programmability in the production of useful materials, which is generally lacking in many molecule-based materials systems. Block copolymers are one molecule that can be programmed to self-assemble, but chemists have been looking to biological molecules (peptides, proteins, deoxyribonucleic acid (DNA), peptide nucleic acids, and others), which have evolved to self-assemble naturally.<sup>1</sup> The rules for protein assembly are complex and make proteins less likely as functional nano-

materials. However, DNA and peptide assembly rules are much simpler. Materials scientists have focused on using DNA and peptides to make structures and scaffolds with biological and medical utility. Precise control and placement of biological molecules has also been difficult. Orienting molecules on surfaces to generate arrays with dense features has been a goal for materials scientists.

**Objective:** This Multidisciplinary University Research Initiative (MURI) studied the nature and rules of self-assembly of biological molecules. The researchers are pioneers in this field, having

developed most of the tools and materials studied in this MURI during previous efforts.<sup>2,3</sup> They studied various biological molecule-based materials including self-assembling peptide nanotubes, collagen-derived peptides, and peptide amphiphiles. They worked to understand the mechanism for self-assembly and the improvement of the material's desired properties. A complementary effort of computational modeling to understand molecular self-assembly was also performed.

Achievements: The utility of the so-called Dip-Pen Nanolithography (DPN) technique was demonstrated and refined during this MURI. Arrays of tobacco mosaic virus (see Figure 1), peptide amphiphiles, and antibodies to the p24 protein of the human immunodeficiency virus (HIV) were patterned onto surfaces via DPN. The p24 antibody array was used as an HIV sensor, and the other two arrays were used to study biological interactions of various molecules. Many other nonbiological nanostructures were produced for the development of functional materials. DPN was used to construct chemical nanosensors, nanoelectrodes, and conducting polymers.



Figure 1. Atomic Force Microscope Images and Height Profiles of a Perpendicular Single Tobacco Mosaic Virus Nanoarray

Two major developments occurred during this MURI. First, the technique of On-Wire Lithography (OWL) was developed (see Figure 2), which produces one-dimensional metallic nanowires with programmable gaps of five to several hundred nanometers. Second, peptide amphiphile nanofibers were developed that self-assemble at low pH. The peptide sequence is capable of

Surface-Templated Bio-Inspired Synthesis and Fabrication of Functional Materials (2000–2005)

Professor Chad A. Mirkin Department of Chemistry Northwestern University

Sponsor: Air Force Office of Scientific Research Dr. Hugh C. DeLong

<sup>&</sup>lt;sup>1</sup> Paul Alivisatos et al., "From Molecules to Materials: Current Trends and Future Directions," *Advanced Materials* 10, no. 16 (1998): 1297–1336.

<sup>&</sup>lt;sup>2</sup> Jeffrey D. Hartgerink et al., "Self-Assembling Peptide Nanotubes," *Journal of the American Chemical Society* 118, no. 1 (1996): 43–50.

<sup>&</sup>lt;sup>3</sup> Richard D. Piner et al., "Dip-Pen' Nanolithography," *Science* 283, no. 5402 (29 January 1999): 661–663.



being modified to produce fibers with variable recognition sites on its surface. These peptides have been used to mineralize inorganic substances such as hydroxyapatite to mimic materials seen in bone.<sup>4</sup>

**Long-Term Significance:** The peptide materials studied in this MURI have provided insight into the field of molecular self-assembly in biological molecules. Peptide nanotubes can be programmed with many useful properties (optical, piezoelectric, and so forth).<sup>5</sup> Peptide amphiphiles can be functionalized to bind a variety of molecules to serve as a scaffold or matrix to grow tissues and bone and therefore have potential for regenerative medicine.<sup>6</sup>

This MURI made progress in the development of techniques to pattern and present biological molecules on surfaces. DPN has been refined to accept multiple molecular inks and has been shown to have multiple applications, including the patterning of chemicals and macromolecules. Molecular biological sensors have

Impact

- Development of OWL
- Developed peptide amphiphile nanofibers
- First FDA approved process for medical test for Coumadin level

been developed with arrays of antibodies. The development of OWL is proving to have a big impact in the field of Surface-Enhanced Raman Scattering<sup>7</sup> and other sensing applications.<sup>8</sup>

Based on this research, the first Food and Drug Administration (FDA)-approved process for medical test for levels the blood thinner Coumadin was developed. Also, this technology led to an extremely sensitive test for prostate-specific antigen (PSA) levels. In addition, the technology was used to develop water testing kits for the Department of Homeland Security (DHS) to look for infectious diseases such as anthrax and tularemia to alert the potential use of those bacteria as bioweapons.

The research from this MURI produced 101 peer-reviewed journal articles, 2 book chapters, and 100+ conference presentations. This MURI also supported 25 graduate students and 31 post-doctoral fellows. One further testament to the significance of this MURI and a prior MURI is the selection of Chad Mirkin as the first double recipient of the prestigious DoD-sponsored National Security Science and Engineering Faculty Fellow (NSSEFF) Award.

**Impact on DoD:** Biological materials with unique properties and the ability to self-assemble could allow a bridging with nanoscale devices. Biological control of nanoscale devices is a concept that is important to and is being considered by DoD. The development of peptide materials into products for regenerative medicine could impact wound healing and combat medical care. OWL is certainly showing progress in the sensing arena, which may advance chemical and biological defense, one of the most important DoD missions since biological and chemical agents are considered "weapons of mass destruction."

<sup>&</sup>lt;sup>4</sup> Jeffrey D. Hartgerink et al., "Self-Assembly and Mineralization of Peptide-Amphphile Nanofibers," *Science* 294, no. 5547 (23 November 2001): 1684–1688.

<sup>&</sup>lt;sup>5</sup> G. Rosenman et al., "Bioinspired Peptide Nanotubes: Deposition Technology, Basic Physics, and Nanotechnology Applications," *Journal of Peptide Science* 17, no. 2 (2011): 75–87.

<sup>&</sup>lt;sup>6</sup> Honggang Cui, et al., "Self-Assembly of Peptide Amphiphiles: From Molecules to Nanostructures to Biomaterials," *Journal of Peptide Science* 94, no. 1 (2010): 1–17.

<sup>&</sup>lt;sup>7</sup> Rebecca S. Golightly et al., "Surface-Enhanced Raman Spectroscopy and Homeland Security: A Perfect Match?," ACS Nano 3, no. 10 (2009): 2859–2869.

<sup>&</sup>lt;sup>8</sup> Adam B. Braunschweig et al., "Nanostructures Enabled by On-Wire Lithography (OWL)," *Chemical Physics Letters* 486, nos. 4–6 (2010): 89–98.

## **Tunable Optical Polymer Systems**

Chromogenic materials are a class of materials whose optical properties change under the influence of external stimuli. These materials are classified by the type of stimuli involved. For example, electrochromism, photochromism, thermochromism, piezochromism, and magnetochromism involve color changes induced by applied electric, optical, thermal, pressure, and magnetic fields, respectively. Photochromism and electrochromism in polymeric and organic materials have been widely investigated and have found application in areas such as self-adjusting sunglasses, filters for optical sensors, medical thermographic recording media, self-adjusting rear view car mirrors, and color-switching ski jackets. However, the full potential of chromogenic materials (e.g., in large-area Tunable Optical Polymer Systems (2000–2004) Professor Samson Jenekhe Department of Chemical Engineering University of Washington

Army Research Office Dr. Douglas Kiserow

information display, optical information storage, holographic recording, smart windows, and photoresistive transducers) has not been realized. The barriers to achieving large-scale and high-impact technological applications of various chromogenic materials include characteristics such as stability of materials under long-term cycling, the speed with which optical changes can be effected, the amount of energy required to achieve optical tunability, satisfactory color contrasts, durability, the processability of the chromogenic materials into suitable forms (conformal coatings, multilayers), and the realization of a variety of necessary properties beyond optical tunability (e.g., mechanical strength).

**Objective**: This Multidisciplinary University Research Initiative (MURI) investigated tunable optical polymer systems suitable for large-area color-switchable coatings and devices, displays, sensors, and other electronic applications. The researchers sought to expand the knowledge base for the design, synthesis, processing, and characterization of new generations of optically tunable polymeric materials suitable for various photonic and optoelectronic applications; develop a fundamental understanding of the physical and chemical mechanisms underlying the chromogenic phenomena, especially electrochromism, photochromism, photoelectrochromism, thermochromism, tunable luminescence, and tunable reflection in polymeric materials; and incorporate these materials into device structures to evaluate their performance. To achieve these objectives, the electronic and molecular structures of several new optically tunable polymer systems were explored.

Accomplishments: Among the many achievements of this MURI, one had considerable significance to DoD. Massachusetts Institute of Technology (MIT) researcher Tim Swager synthesized novel fluorescent polymers capable of detecting toxic chemical vapors in air at trace concentration levels. Thin films of these polymers contain receptor sites designed to interact specifically with a target (such as a nitroaromatic explosive), thus enhancing the selectivity of the polymer to this target. As illustrated in Figure 1, connecting the fluorescent polymers via a conjugated molecular network led to an amplification effect responsible for exceptional sensitivity to and the ability to discriminate between target molecules. This sensitivity has been successfully applied as explosive and chemical detectors.



Figure 1. Indicator That Undergoes Highly Sensitive Fluorescence and Adsorption Responses Shown to Reactive Phosphates

**Long-Term Significance:** Swager's work highlighted was patented by MIT and licensed to Nomadics Inc. The technology was purchased from Nomadics by ICx and then sold to FLIR Systems, who now sells a line of explosives detectors, under the name of FIDO<sup>®</sup> (see Figures 2 and 3), based on the technology developed by this MURI. Originally developed to detect nitroaromatic explosives such as trinitrotoluene (TNT), the FIDO<sup>®</sup> sensor demonstrated a lower detection limit of 1 femtogram of TNT in laboratory tests. Further advancements



- Synthesis of fluorescent polymers that detect toxic chemical vapors
- FIDO<sup>®</sup> line of handheld explosives detectors

have led to the detection of other explosive compounds, such as Research Department Explosive (RDX), pentaerythritol tetranitrate (PETN), and nitroglycerin (NG). The FIDO<sup>®</sup> product line came several years after this MURI ended and represents a significant military and national security application that was derived from this basic research.



Source: <u>http://gs.flir.com/</u>. Figure 2: FIDO<sup>®</sup> X3 Handheld Explosives Detector (Right) and Amplifying Fluorescent Polymers (Left)

Note for Figure 2. The FIDO<sup>®</sup> X3 Handheld Explosives Detector relies on amplifying fluorescent polymers (left) under an exclusive license from MIT.



Source: <u>http://gs.flir.com/</u>. Figure 3. FIDO<sup>®</sup> Technology Used on a Robotic Device

Note for Figure 3. FIDO<sup>®</sup> technology has been designed for ease of operation and is suitable for handheld, bench-top, and robot-mounted applications.

The research from this MURI resulted in 4 patents and 33 derived patents. Also, the MURI team produced 76 publications that generated over 5,000 citations. In addition, this MURI supported 7 faculty, 24 graduate students, 26 post-doctoral fellows, and 5 undergraduate students.

**Impact on DoD:** Explosives continue to be a favored weapon of terror and destruction. Professor Swager's novel fluorescent polymer materials that undergo rapid, easily detectable responses to toxic chemicals were a crucial first step in the development of the handheld FIDO<sup>®</sup> explosive detectors. As a trace detector for explosive vapor, FIDO<sup>®</sup> has several forensic, humanitarian, and military improvised explosive device (IED) applications. FIDO's<sup>®</sup> portability and sensitivity, combined with the ability to be integrated with many types of remote vehicles, allow it to be deployed in ways never before possible. The U.S. military is currently using FIDO<sup>®</sup> for explosive detection operations at home and abroad.

## **Center for Advanced Nitride Electronics (CANE)**

Wide-bandgap semiconductors, such as gallium nitride (GaN), promise new devices that are likely to significantly impact areas such as high-speed communications, advanced radar, and power control and switching. The material properties of these semiconductors make them well suited to operation at high temperatures and frequencies and at electrical current or voltage levels inaccessible to standard silicon-based electronics. That said, in the late 1990s, significant challenges remained, including film quality and device performance.

**Objective:** The objective of this Multidisciplinary University Research Initiative (MURI) was to develop Center for Advanced Nitride Electronics (CANE) (2001–2006)

Professor Umesh K. Mishra Department of Electrical and Computer Engineering University of California, Santa Barbara

> Sponsor: Office of Naval Research Dr. Paul Maki

or significantly improve the fundamental scientific understanding of the physical mechanisms governing noise behavior in GaN-based transistors and circuits. The focus was on improving GaN devices in terms of linearity, gain saturation, power density, and microwave, white, and 1/f noise. This research brought GaN from the realm of a "promising material" to the "material of choice" for high-frequency and high-power devices. University participants included the University of California, Santa Barbara, the California Institute of Technology, the University of Michigan, The Ohio State University, Wright State University, and the Virginia Polytechnic Institute and State University.

Achievements: GaN-based transistors offer the unique advantage of simultaneously achieving high power and low noise from amplifiers. Low-noise operation is critical for certain types of commercial and military radar systems. For example, the ability to detect distant objects is ultimately linked to the electronics' signal-to-noise performance. The research done during this MURI separated the impact of the underlying materials, device design, and circuit topology on noise and subsequently improved the state of the art in each of these areas, thereby significantly improving the amplifier's overall noise performance. Much of this progress came from improvements in the growth of the GaN materials themselves. These improvements resulted in improved wafer uniformity, breakdown



Figure 1. Scanning Electron Microscope (SEM) Image of 4 × 50 μm HEMT with Four gate Fingers, Each 50-μm Wide

voltage, and defect density. Using a unique device design involving field plates, this MURI increased the power density of GaN High Electron Mobility Transistors (HEMTs) (see Figure 1) from roughly 4 W/mm to 26 W/mm.

**Long-Term Significance:** Under CANE, various current and voltage "chokes" were identified, which allowed the optimization of the overall device. The chokes, if not eliminated, severely limit the gain in these devices. The commercial significance is apparent in that 11 companies worldwide are involved with GaN power electronic devices, and CANE was the first effort worldwide that showed one could produce kilovolt-class GaN materials. Of particular significance was a materials breakthrough by one of the MURI participants involving the development of an aluminum nitride (AlN) barrier layer technology designed to be adjacent to the GaN

channel. This development dramatically increased the sheet charge density and the mobility in the materials and is now commonly used for all GaN power devices.

Approximately 35 students were trained during this MURI, many of whom went on to jobs in leading industrial and government research labs and to positions in top universities across the nation.

**Impact on DoD:** The results from this MURI will significantly impact a wide range of U.S. military systems. The goal of the program was to gain a better understanding of the



Figure 2. A Two-Stage High-Gain, High-Power Distributed Amplifier Using Dual-Gate GaN HEMTs mechanisms governing noise behavior in GaN-based transistors and circuits. The resulting lownoise, highspeed, and high-power

#### Impact

- Demonstrated significant improvements in the growth of the GaN, resulting in improved wafer uniformity, breakdown voltage, and defect density
- Developed a unique AIN barrier layer technology for use in GaN HEMTs
- Demonstrated a new GaN HEMT design resulting in significant improvements in device linearity, gain saturation, power density, and noise
- First demonstration of kilovolt-class GaN materials for high-power electronics

devices, circuits and amplifiers (see Figure 2) will find application in electronic warfare, highfrequency radars, and in numerous high-power applications. This type of semiconductor also performs well in high-temperature environments.

The significance of this MURI to DoD will continue to increase as this technology begins to be fielded in numerous U.S. military systems.

## **Optical Frequency Combs**

An optical frequency comb is a pulsed laser that generates millions of equally spaced colors of visible light. These equally spaced intervals can be used like a ruler for extremely accurate measuring of time or distance. The seminal work on laser-based optical combs by Theodor W. Hänsch and John L. Hall was one of the achievements that led to their Nobel Prize in 2005. In developing a measurement technique known as the "optical frequency comb," they have made it possible to measure light frequencies to an accuracy of 15 significant digits. The comb exploits the interference of lasers of different frequencies, which produces sharp,



femto-second pulses of light at extremely precise and regular intervals and allows precise measurements to be made of light of all frequencies. This development has many applications in fundamental and applied fields.

**Objective:** For this Multidisciplinary University Research Initiative (MURI), principal investigator (PI) Professor Jun Ye set out to demonstrate the feasibility of extending frequency comb technology from the optical into the extreme ultraviolet (XUV) realm. The main motivation for this MURI was to extend high-precision laser-spectroscopy techniques and high-resolution quantum control into the ultraviolet (UV) regime—which would revolutionize precision measurement of many ground state transitions of atoms and molecules. Ye believed that this research would make progress toward an important overarching goal: extending frequency comb technology to access every frequency range in the entire electromagnetic (EM) spectrum, with revolutionary measurement precision.

Achievements: Building a pulsed XUV laser stable enough to create a frequency comb is difficult. Ye and his team developed an alternate approach to this challenge: use of a high-power, high-repetition pulsed infrared (IR) laser coupled into an enhancement cavity. This enhancement cavity was engineered to add laser pulses constructively. After repeated round trips through the enhancement cavity, the original laser pulse would build up intensity that was high enough to generate high-frequency photons that were harmonics of the original pulse.

Ye's group continued to develop novel enhancement cavity designs, improving on the performance of the first. They showed that a fiber-based mode-locked laser (10 W Yb) could be used to achieve higher average and peak power.<sup>1</sup> With this new source, they produced harmonics up to the twenty-first (the cutoff in Xenon) with 0.1 to 10  $\mu$ W of average power per harmonic, as shown in Figure 1. This increase in average power per harmonic allowed the observation of quantum interference between different electron trajectories in the high-harmonic generation (HHG) process and, importantly, enabled the demonstration of comb coherence for the first time (see Figure 2).

Ye's group also conducted a series of experimental measurements of trace gas detections and human breath analysis and demonstrated the characterization of cold molecular beams. These results demonstrated clearly that the wide bandwidth and ultra-sensitive nature of the femto-second enhancement cavity enables powerful real-time detection and identification of many molecular species in a massively parallel fashion.

<sup>&</sup>lt;sup>1</sup> R. Jason Jones et al., "Phase-Coherent Frequency Combs in the Vacuum Ultraviolet via High-Harmonic Generation Inside a Femtosecond Enhancement Cavity," *Physical Review Letters* 94, no. 19 (2005): 193201-1–193201-4.



Source: The results in Figure 1 are presented in Yost, D. C. et al. 2008. "Efficient Output Coupling of Intracavity High-Harmonic Generation." *Optics Letters* 33 (10): 1099–1101.

#### Figure 1. Experimentally Observed Spectrum Using Xenon Representing the First Demonstration of the Seventeenth Through the Twenty-First Harmonic Using Intracavity HHG



Source: http://jila.colorado.edu/yelabs/news/indomitable-ruler-light.

Figure 2. World's First XUV Frequency Comb

Note for Figure 2: This MURI created the world's first measurement ruler for light in the XUV.

This MURI demonstrated the feasibility of XUV frequency combs, which, for the first time, had sufficient power for real applications.<sup>2</sup>

**Long-Term Significance:** The potential applications from this advance in capability range from basic research problems in physics, such as precise measure of physical constants, to diverse commercial applications. Multiple companies are now building spectroscopic instrumentation and measurement tools using the techniques first proposed in this MURI. These companies include Agilent Technologies, Vescent Photonics, Precision Photonics, and INCA America (mode pulsed lasers).

The availability of commercial instruments is facilitating the evolution of new applications, ranging from fundamental research to telecommunications and satellite navigation. Laser frequency combs provide the long-missing clockwork for optical atomic clocks. Laser combs are revolutionizing molecular spectroscopy by dramatically extending the resolution and recording

<sup>&</sup>lt;sup>2</sup> Arman Cingöz et al., "Direct Frequency Comb Spectroscopy in the Extreme Ultraviolet," *Nature* 482 (02 February 2012): 68–71.

speed of Fourier spectrometers. The calibration of astronomical spectrographs with laser combs will enable new searches for earth-like planets in distant solar systems and may reveal the continuing expansion of space in the universe. Very sensitive spectrometers that can measure molecules present in air in parts per billion (ppb) can be used to screen patients based on the smell of their breath.

By comparing with theoretical calculations, these experiments might allow for some of the most stringent tests ever applied to quantum electrodynamics. The production of vacuum ultraviolet (VUV) and XUV frequency combs also represents pro-

#### Impact

- World's first measurement ruler for light in the XUV
- Leading edge in U.S. technology being sustained for the next generation of commercial and military communications

gress toward an ongoing goal: to use frequency comb technology to access every frequency range in the EM spectrum, with revolutionary precision. This work will also dramatically enhance the efficiency or coherence of the next-generation accelerator-based advanced light sources.

**Impact on DoD:** The impact of this basic research on DoD is diverse and potentially significant. The new ruler may make possible the development of new clocks based on the behavior of nuclei of atoms. The precision clocks used in today's Global Positioning System (GPS) were initially developed as laboratory standards. The global telecommunications network will require ever more precise clocks as data rates increase. Using optical frequency combs, improvements in bandwidth are possible for optical communications systems.

The development of sensitive spectrometers also aids in the area of bio threat detection. The Defense Threat Reduction Agency (DTRA) is funding applications to look for explosive trace gases and to view bacteria without killing them.

## **Center for Photonic Quantum Information Systems**

Building a quantum computer (QC) is one of the grand challenges of the twenty-first century. A QC represents a new paradigm of computation based on some fundamental and strange operational features of quantum mechanics (QM) that can be applied to a quantum bit or qubit. A qubit is a single quanta of a two-level quantum system. Prototypical qubits are, for example, the spin of an electron (either up or down) or the polarization of a photon (either vertical or horizontal). The two very strange and fundamental quantum mechanical operations are called superposition and entanglement. Superposition means that a single qubit can be put into a state that is a linear combination of

Center for Photonic Quantum Information Systems (2003–2009)

Professor Jelena Vuckovic Department of Electrical Engineering Stanford University

> Sponsor: Army Research Office Dr. T. R. Govindan

spin up and spin down states. This is non-Boolean and implies that the electron can be in both states simultaneously, clearly a non-classical consequence of QM. Entanglement implies that the quantum states of two or more qubits can be intertwined so that a measurement on one qubit, which itself is in a superposition state, determines the state of the other qubit or qubits despite the fact that the qubits can be very far apart. It is these "spooky" properties that make this area so appealing. In fact, Einstein never really believed in entanglement and actually called it "spooky action at a distance." The simplest QC is a Quantum Repeater, which allows for ultra-secure communications and requires only a handful of qubits. A QC can also do problems, such as factoring very large numbers. For a conventional computer, this problem grows exponentially with the number of bits in the number to be factored. In a QC, the problem can be solved with an exponentially smaller number of qubits. Although building a QM factoring machine is still at least a decade away, this problem has attracted some of the best minds in the world. The principal investigator (PI) and co-PIs supported in this Multidisciplinary University Research Initiative (MURI) are some of the best minds working on developing the needed infrastructure to make a QC possible, and this MURI has produced some significant technology that will accelerate the development of a Quantum Repeater in the near term and a full QC in the far term.

**Objective:** The goal of this MURI was the development of several key photonic quantum technologies that will provide some of the needed infrastructure that will be essential for building complete quantum systems in the future.

Achievements: Some of the photonic quantum technologies developed during this MURI include single-photon and entangled-photon sources based on quantum dots in photonic bandgap cavities, novel qubits, and qubit gates based on electrons in quantum dots and nitrogen vacancy (NV) defect centers in diamond. These gates are needed to entangle the qubits. This MURI also developed a quantum memory using unique optical storage techniques and single photon detectors, including superconducting bolometric detectors, which are currently the best photon counters in existence.

**Long-Term Significance:** This MURI demonstrated all of the devices that were proposed. Having a heralded tunable single photon source (a heralded source is a photon on demand) is a key element for any optically based QC architecture, and several different sources were explored in this MURI, all with a considerable degree of success. Figure 1 shows an example of one of the more sophisticated structures demonstrated by the PI and several of her co-PIs, which illustrates several tunable photon sources consisting of a quantum dot in a two-dimensional (2D) photonic crystal cavity resonator.



Source: Vuckovic, Jelena, and Paul Kwait. 2009. MURI. Center for Photonic Quantum Information Systems: Scientific Progress and Accomplishments. Research Triangle Park, NC: U.S. Army Research Office, 27.

#### Figure 1. (a) Fabricated Structure for Laser-Induced Selective Tuning of a Quantum Dot in a Photonic Cavity by Local Heating; (b) Selective Tuning on a Single Indium Arsenide/Gallium Arsenide (InAs/GaAs) Quantum Dot by This Technique

Note for Figure 1: In (a), the device consists of a photonic crystal cavity with embedded quantum dot and heating pad next to them. The heating pad is made of a layer of chromium/gold (Cr/Au) deposited on GaAs, and the structure is tuned by illumination with a 960-nm continuous wave laser.

Several other sources of single photons were demonstrated, including impurity-based single photon sources, parametric down-conversion sources for entangled photon pairs, and a microstructure fiber-based two-photon source. Another key component for any quantum information system is a fast single photon counter, and this MURI demonstrated several schemes for enhancing the counting rate of single photon detectors.

This MURI, which concluded in 2009, has had a significant impact on the field of quantum information systems. The research from this MURI produced 32 peer-reviewed papers, many in the most highly cited journals (e.g., *Nature* and *Science*), and 13 conference papers. Many of the papers already have well over 100 citations. The grant supported

Impact

- Development of single-photon and entangled-photon sources
- Development of solid-state
  quantum gates based on
  quantum dots and on NV
  centers in diamond
- Development of quantum memories using optical storage systems
- Development of high-efficiency single-photon detectors

11 graduate students 1 post-doc, 3 research scientists, and 2 undergraduate students.

**Impact on DoD:** This project is important for DoD because all of the encryption technology used by DoD is based on the difficulty of factoring a very large number. Conventional computers cannot factor a number of over 1,000 bits in any reasonable time frame, whereas a QC will be able to factor this number in a matter of hours. A QC can also search large databases much faster than conventional computers can, and significant potential also exists for large QCs to also be able to process images and signals much faster. DoD is currently investing significant resources to develop the infrastructure for quantum communication and quantum computation.

# **Correlation between Physicochemical Characteristics and Toxicological Properties of Nanomaterials**

The rapidly emerging field of nanotechnology has led to an explosion of newly fabricated nanomaterials (less than 100 nm) with properties unlike their respective bulk materials. These nanostructure-dependent properties (i.e., chemical, mechanical, electrical, optical, magnetic, or biological) have suitability for a variety of commercial and military applications.<sup>1</sup> The topic of nanomaterials, with their unique, highly desired properties, has generated considerable commercial interest. Running counter to that drive to develop and produce commercial nanomaterials quickly, a small number of scientists cautioned that these nanomaterials may also possess "nanostructure-dependent biological activ-

Correlation between Physicochemical Characteristics and Toxicological Properties of Nanomaterials (2004–2011)

Professor Günter Oberdörster Department of Environmental Medicine University of Rochester

Sponsor: Air Force Office of Scientific Research Dr. Patrick Bradshaw

ity."<sup>2</sup> These scientists advocated a better understanding of nanotoxicology, which can be defined as the "safety evaluation of engineered nanostructures and nanodevices."<sup>3</sup>

In the early 1990s, Dr. Oberdörster was one of a group of researchers to show that manufactured nanoparticles induce a greater inflammatory response on lung tissue than larger particles<sup>4</sup> and that these nanoparticles are involved in epithelial translocation.<sup>5</sup> Before this early research, the notion that these small particles could create such significant effects was viewed with much skepticism. This Multidisciplinary University Research Initiative (MURI) was fueled by this uncertainty and the need to address important issues with regard to nanomaterial safety.

Although humans have been exposed to airborne nanosized particles (NSPs) throughout their evolutionary stages, such exposure has increased dramatically over the last century due to anthropogenic sources. The rapidly developing field of nanotechnology is likely to become yet another source through inhalation, ingestion, skin uptake, and injection of engineered nanomaterials. Information about safety and potential hazards is urgently needed. Although many uptake and translocation routes have been demonstrated, others still are hypothetical and need to be investigated. Translocation rates are largely unknown, as are the accumulation and retention in critical target sites and their underlying mechanisms. These mechanisms, as well as potential adverse effects, largely depend on physicochemical characteristics of the surface and core of NSPs. Both qualitative and quantitative changes in NSP biokinetics in a diseased or compromised organism also need to be considered. See Figure 1.

**Objective:** The goal of this MURI was to determine the toxicity of nanomaterials in relation to their physicochemical characteristics. Scientists at the University of Rochester, the University of Minnesota, and Washington University in St. Louis investigated protein/nanoparticle interactions, intracellular motion of nanoparticles, characterization of engineered nanomaterials (mostly commercial sources), and the synthesis of nanomaterials for biological studies and animal inhalation exposure studies via newly developed electrospray based delivery systems.

<sup>&</sup>lt;sup>1</sup> Günter Oberdörster et al., "Principles for Characterizing the Potential Human Health Effects from Exposure to Nanomaterials: Elements of a Screening Strategy," *Particle and Fiber Technology* 2, no. 8 (2005): 2.

<sup>&</sup>lt;sup>2</sup> Ibid., 2.

<sup>&</sup>lt;sup>3</sup> Günter Oberdörster et al., "Nanotoxicology: An Emerging Discipline Evolving from Studies of Ultrafine Particles," *Environmental Health Perspectives* 113, no. 7 (2005): 823.

<sup>&</sup>lt;sup>4</sup> G. Oberdörster et al., "Increased Pulmonary Toxicity of Ultrafine Particles? II. Lung Lavage," *Journal of Aerosol Science* 21, no. 3 (1990): 384–387.

<sup>&</sup>lt;sup>5</sup> J. Ferin et al., "Pulmonary Retention of Ultrafine and Fine Particles in Rats," *American Journal of Respiratory Cell and Molecular Biology* 6, no. 5 (1992): 535–542.



Source: Oberdörster, Günter et al. 2005. "Nanotoxicology: An Emerging Discipline Evolving from Studies of Ultrafine Particles." *Environmental Health Perspectives* 113 (7) (July): 836.

#### Figure 1. Biokinetics of NSPs

Achievements: This MURI produced a comprehensive review article<sup>6</sup> on nanotoxicology. This article highlights past and present research of this newly developed field and, to date, has been cited over 2,000 times. *Environmental Health Perspectives* named the article Paper of the Year for 2008 as "the most frequently cited article over the preceding 60 months in the environmental health sciences literature."<sup>7</sup>

Many "firsts" occurred during this MURI. A screening process to assess the hazards of engineered nanomaterials was developed in 2005 by an International Life Sciences Institute (ILSI) Research Foundation/Risk Science Institute, which sponsored a working group of the leading experts in nano-

### Impact

- Developed a screening process to assess the toxicity of nanoparticles
- Dr. Oberdörster coined the term "nanotoxicology"
- Growth of field led to start of the international NANOTOX conference

toxicology.<sup>8</sup> Although the resulting journal article is not attributed directly to this MURI, Dr. Oberdörster is the lead author. Other "firsts" include the 1<sup>st</sup> International Conference on Nanotoxicology (NANOTOX 2006). Dr. Oberdörster was the keynote speaker at NANOTOX 2010. The inaugural publication of the journal *Nanotoxicology* occurred in 2007.

**Long-Term Significance:** This MURI produced a paradigm shift in that the interest in nanotoxicology grew substantially during this MURI. A Google Trends search using the word "nanotoxicology" yields the results in Figure 2. It is apparent that the term "nanotoxicology,"

<sup>&</sup>lt;sup>6</sup> Günter Oberdörster et al., "Nanotoxicology: An Emerging Discipline Evolving from Studies of Ultrafine Particles," *Environmental Health Perspectives* 113, no. 7 (2005): 823–839.

<sup>&</sup>lt;sup>7</sup> Günter Oberdörster et al., Correlation between Physicochemical Characteristics and Toxicological Properties of Nanomaterials, Rochester MURI Project – Progress Report: September 1, 2007 to August 31, 2008, Award Number FA9550-04-1-0430 (Rochester, NY: University of Rochester), 8.

<sup>&</sup>lt;sup>8</sup> Günter Oberdörster et al., "Principles for Characterizing the Potential Human Health Effects from Exposure to Nanomaterials: Elements of a Screening Strategy," *Particle and Fiber Technology* 2, no. 8 (2005): 1–35.

originally coined in a commentary on nanotechnology in 2004,<sup>9</sup> has gained widespread interest. It appears that the "spike" at 2007 coincides with the first publication of *Nanotoxicology*.



Figure 2. Google Trends Search for Nanotoxicology

**Impact on DoD:** DoD has a long-term interest in medical science advances that can be used to protect and restore the health of its large workforce. Nanoparticles can be tailored for wide-ranging applications in the diagnosis and treatment of many diseases. Therefore, it is important to DoD (and to the rest of the non-military population) to understand the potential unintended consequences of these treatments. DoD, in funding this MURI, chose to assume responsibility to apply novel medical technologies wisely.

<sup>&</sup>lt;sup>9</sup> Robert F. Service, "Nanotechnology Grows Up," *Science* 304, no. 5678 (18 June 2004): 1732–1734.

## Laser-Addressed Atomic Micromagnetometers

Magnetism and magnetic fields are ubiquitous in nature, and being able to measure ultra-small differences in magnetic fields is the key to many diverse applications, from imaging the body through Magnetic Resonance Imaging (MRI) to locating buried magnetic objects such as explosives, mines, and submarines. Magnetic materials and magnetic fields are measured by magnetometers, and this Multidisciplinary University Research Initiative (MURI) has significantly enhanced the state of the art by developing the world's most sensitive magnetometers with sensitivities less than a femtotesla  $(10^{-15} \text{ T})$ , making them much more sensitive than superconducting magnetometers, which,

Laser-Addressed Atomic Micromagnetometers (2005–2011)

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> Sponsor: Office of Naval Research Dr. Michael Shlesinger

until recently, were the most sensitive detectors of magnetic fields. These new ultra-sensitive magnetometers are based on the effect of magnetic fields from the spins of a vapor of alkali atoms (e.g. sodium, potassium, rubidium) that have been pre-aligned using a novel optical technique involving circularly polarized light (pump laser). A magnetic field causes the direction of the spins to rotate (precess) and this rotation is in turn detected by a probe laser. This technique is illustrated in Figure 1.



Source: http://newscenter.lbl.gov/2010/09/14/putting-a-spinon-light-and-atoms/.

#### Figure 1. Schematic of a Laser-Addressed Atomic Magnetometer

**Objective:** The goal of this MURI was to exploit several discoveries made that, together, had a tremendous impact on the state of the art of atomic vapor magnetometers. This MURI brought together groups with strong expertise in complementary areas, including modulated-light non-linear magneto-optical rotation (Berkeley), spin-exchange-relaxation-free (SERF) magnetometry (Princeton, Physics), surface-science expertise (Princeton, Chemistry). It also benefitted from the expertise of the MURI partners: microfabricated atomic devices (National Institute of Standards and Technology (NIST)), and Navy implementations (Navy Laboratory at Patuxent Naval Air Station). This combination has resulted in extremely productive cross-pollinating research that resulted in the most sensitive magnetometers ever built.

Achievements: The sensitivity of an atomic vapor magnetometer is almost entirely based on the time that the pre-polarized ensemble of alkali atoms in the vapor cell maintain their degree of polarization in the absence of any magnetic field (relaxation time). This MURI team combined several major discoveries to develop the most advanced vapor magnetometer ever built. One of the major relaxation mechanisms is collisions of the alkali atoms with the wall of the vapor cell. The Berkeley group working with (unfunded) collaborators in St. Petersburg, Florida, discovered a family of anti-relaxation coatings that have extended the spin relaxation time by several orders of magnitude. These coatings were significantly enhanced in collaboration with the Princeton Chemistry team members, who found related compounds that enhanced the lifetime even further. The Physics group at Princeton added another technique to further enhance the lifetime using a technique called SERF. This technique added a buffer gas to the cell and, at the same, time

increased the temperature of the cell. This technique reduces collisions with the walls and increases the collisions within the cell. The inter-cell collisions reinforce the polarization, whereas the number of collisions with the walls is reduced. The end result is an even longer relaxation time and a magnetic field sensitivity of 160 attotesla  $(10^{-18})$  per root Hertz at one Hertz almost two orders of magnitude better than the best superconducting magnetometer.



Source: http://www.twinleaf.com/magnetometer/vector/SERF-2/.

Figure 2. An Ultrasensitive Compact Vector Magnetometer using SERF Produced by Twinleaf

members, students, and postdocs moved on to work in related efforts at Los Alamos National Laboratory (LANL) and companies such as Geometrics and AOSense. Overall, this MURI supported 20 graduate students and 7 postdocs, and the research from this MURI at least 10 patents and more than 50 publications with over 2,000 citations.

**Impact on DoD**: The military implications of this technology are widespread, based on DoD's requirements for locating magnetic objects from standoff distance, which

Long-Term Significance: Magnetometers, using the techniques developed in this MURI, are being used for diverse applications (e.g., fundamental physics experiments, such as determining the electric dipole-moment of the neutron, a Global Network of Optical magnetometers for Exotic Physics (GNOME) looking for exotic transient spin couplings that would violate the standard model of high energy physics; a remote magnetic mapping of the mesosphere; and novel applications for MRI). These magnetometers are now being produced commercially by several spinoffs, including a Princeton-based company, Twinleaf LLC, which produces precision magnetic field sensors based on this MURI work (see Figure 2).

## Impact

- Enables fundamental Physics
  experiments
- Most sensitive magnetic sensors
- Novel applications enables ultrahigh sensitivity
- New methods for standoff
  detection of magnetic objects

involves detection and location of mines, improvised explosive device (IEDs), and submarines. In particular, anti-submarine warfare (ASW) is based on magnetic anomaly detection using highly sensitive magnetometers, and this MURI had an implicit goal of improving sensors for ASW. The Navy, has continued this work, with several Small Business Innovation Research (SBIR) projects. A strong connection also exists with the Navy Laboratory at Patuxent Naval Air Station.

Several

MURI

## **Microvascular Autonomic Composites**

Structural polymers and composite materials are susceptible to damage in the form of cracks deep within the structure, making them difficult to detect and repair. Professor Scott White and his team at the University of Illinois at Urbana-Champaign pioneered work in structural polymeric materials with the ability to heal cracks autonomically.<sup>1</sup> Microcapsules of a healing agent (dicyclopentadiene (DCPD)) within the material rupture upon damage to the material. An embedded catalyst (Grubbs' catalyst) then triggers polymerization of the healing agent to heal the damaged material. However, this microcapsule method of delivering the healing agent allows only a single repair

Microvascular Autonomic Composites (2005–2011)

Professor Scott White Department of Aerospace Engineering University of Illinois at Urbana-Champaign

Sponsor: Air Force Office of Scientific Research Dr. Byung-Lip Lee

and thus provides a limited solution for materials that undergo continuous stress and multiple opportunities to incur damage.

**Objective:** This Multidisciplinary University Research Initiative (MURI) employed a biomimetic approach (see Figure 1) to material healing to expand on the original work of the principal investigator (PI). The concept was to integrate composite material systems with threedimensional (3D) microvascular network architectures to deliver healing agents in an imitation



Figure 1. The MURI's Biomimetic Approach

Note for Figure 1: This MURI used biomimetic and bioinspired designs and brought together the acknowledged leaders of this field of research and the foremost scientists and engineers in autonomic materials. of the self- generation mechanisms of biological systems.

Achievements: This MURI developed a chemical method of monitoring the healing process through the production of a fluorescent reporter. The researchers studied alternative catalysts, improving thermal stability of microcapsules and investigating solventbased healing molecules. The air sensitivity and cost of the catalyst were also addressed.

To allow multiple of cycles of healing at a particular point in the material, the group developed methods of printing microvascular networks and supporting them with pumping and valving structures that were capable of delivering healing agents to multiple points within the material. They were able to demonstrate multiple cycles of healing with the microvascular networks and effective healing in the bulk of the material.<sup>2</sup>

**Long-Term Significance:** Self-healing materials will improve lifetimes, decrease maintenance and costs, and decrease failure rates.<sup>3</sup>

<sup>&</sup>lt;sup>1</sup> S. R. White et al., "Autonomic Healing of Polymer Composites," *Nature* 409 (15 February 2001): 794–797.

<sup>&</sup>lt;sup>2</sup> Andrew R. Hamilton et al., "Self-Healing of Internal Damage in Synthetic Vascular Materials," *Advanced Materials* 22, no. 45 (2010): 5159–5163.

<sup>&</sup>lt;sup>3</sup> Nathalie K. Guimard et al., "Current Trends in the Field of Self-Healing Materials," *Macromolecular Chemistry and Physics* 213, no. 2 (2012): 131–143.

This idea has spawned a large field of self-healing materials that not only respond to fracture or stress, but can respond to heat<sup>4</sup> or be optically activated. A company called Autonomic Materials was formed in 2005 to commercialize the technology developed in the original study by the researchers at University of Illinois at Urbana-Champaign.

The types of materials being studied in the experiments were commercial systems that were used in a broad cross section of industries, including aerospace and microelectronics. The multiple capabilities of the microvascular materials have vari-

#### Impact

- Advancement of the chemistry of healing composite materials
- First demonstration of multiple cycles of healing
- Formed start-up company
  Autonomic Materials

ous applications. The thermal control could be immediately applied in microelectronics and the computer industry. The structural applications of microvascular materials could be applied in areas such as robotics (via stiffness control of self-healing) or an aircraft airframe that has to endure repeated cycles of stress, vibration, and temperature changes.

The research from MURI resulted in four patents and eight derived patents, and some additional patents are pending. Also, the MURI team produced 50 publications that generated 6,549 citations.

**Impact on DoD:** DoD has an interest in self-healing structures because military equipment is subjected to great stress that may cause structural breakdown. Methods that would allow a structure to self-heal could greatly reduce the need for repair and maintenance. Increasingly, the Services are employing composite materials as structural components in complex aircraft. While composite materials may be stronger and more lightweight than traditional metals, composite materials are susceptible to damage due to impact from stressful use. Currently, if a composite structure is damaged, it must be pulled out of service for repair. A self-healing composite is a highly desired functionality for each of the Services in DoD.

Based on the results of this MURI, at least four Small Business Innovative Research (SBIR) grants have been initiated to develop self-healing and microvascular structured materials further in an attempt to develop prototypes. In addition, some defense contractors are conducting internal research and development (R&D) to analyze the practicality of building aircraft components with self-healing materials based on this MURI.

<sup>&</sup>lt;sup>4</sup> Xiangxu Chen et al., "A Thermally Re-mendable Cross-Linked Polymetric Material," *Science* 295, no. 5560 (1 March 2002): 1698–1702.

## An Integrated Cellular Materials Approach to Force Protection

The development of armor with increased capabilities for protection against the blast and ballistic threats associated with either nearby explosive events or highspeed projectiles is an ongoing concern of the U.S. military. This project was the third in a sequence of innovative armor materials Multidisciplinary University Research Initiatives (MURIs). The first (*Ultra-Light Metal Structures*) was sponsored by the Defense Advanced Research Projects Agency (DARPA) in 1996. This early MURI provided the foundation for the concepts of using cellular materials as very lightweight yet very resistant materials for armor. The principal investigator (PI) was Professor Anthony Evans.

An Integrated Cellular Materials Approach to Force Protection (2006–2011)

Professor Haydn Wadley Department of Materials Science and Engineering University of Virginia

> Sponsor: Office of Naval Research Dr. David Shifler

That MURI was followed by a second MURI (*Ultralight Metallic Panels with Textile Cores Designed for Blast Mitigation and Load Retention*) sponsored by the Office of Naval Research (ONR) starting in 2003, which was led by John Hutchinson (Harvard). That MURI pioneered a multi-layer approach that combined the blast resistance of cellular structures with the impenetrability of novel fabrics and elastomers. The final MURI, the one reported here, developed innovative material combinations and tested the fundamental concepts developed in the earlier MURIs. The key MURI team members—Evans, Hutchinson, and Wadley—were the intellectual drivers of the concept of using cellular materials as the basis for advanced armor and this concept has now been validated for future force protection. See Figure 1.

(a) Honeycomb (square)	(b) Corrugation	(c) Pyramidal	Armored high mobility multi-purpose wheeled vehicle
(d) Tetrahedral	(e) 3D-Kagomé	(f) Diamond textile	
	XAXXXX		
(g) Square Textile	(h) Diamond collinear	(i) Square collinear	111111
			MicroTruss <sup>10</sup> core panel absorbs blast impact

Source: http://www.cellularmaterials.net/blast-protection.html.

Figure 1. Cellular Materials as the Basis for Advanced Armor

Note for Figure 1: The left side shows nine examples of different topologies of cellular lattices, and the right side shows one potential application for vehicle protection.

**Objective:** The overarching objective of this MURI was to use a combination of topology and materials, guided by state-of-the-art simulation tools to establish new force protection concepts that can be adapted to local threat environments. This approach included using emerging multi-layer systems consisting of ultra-light cellular constituents integrated with high specific-strength metallics, ceramics, ballistic fabrics, and elastomers.

Achievements: This MURI established the fundamentals governing the interactions between air blasts and structures as well as the principles of ballistic penetration over very wide velocity regimes. Using these fundamental principles, the team designed and fabricated optimized

composites for various threat environments, developed the procedures for the dynamic testing of these materials, validated the design models in collaboration with the Navy and Army using gas gun testing on unit cells, blast tested large panels, conducted dynamic tearing measurements in shock tubes, and conducted a variety of ballistic tests with spherical projectiles that had impact velocities exceeding 3500 m/s. The results were analyzed and compared with simulations using commercial codes and codes developed in this MURI.

**Long-Term Significance:** This MURI has laid the foundations for the design and manufacture of future generations of armor, specifically for the protection of tactical vehicles for the Army and Navy but also for personnel protection.

This MURI team brought together faculty from the University of Virginia, the University of California, Santa Barbara, Princeton, Harvard, and the Massachusetts Institute of Technology (MIT), working closely with collaborators from the University of Cambridge (separately funded by ONR), the Naval Surface Warfare Center (NSWC) and the Army Research Laboratory (ARL). The goal was to explore new lightweight, volumetrically efficient concepts to enhance projectile impenetrability and blast resistance. The team members were exceptionally distinguished and included three members of the National Academy of Engineering (NAE), two of whom are members of the National Academy of Sciences (NAS)and one of whom is a Fellow of the Royal Society (United Kingdom).

Impact

- Designed and developed simulation for future force protection
- Designed and built optimized armor based on cellular materials
- Empirically validated design concepts

This MURI has produced 66 papers in peer-refereed journals, and these papers have generated over 400 citations.

**Impact on DoD**: The major impact of this MURI for DoD is that it will provide the tools and materials to produce reliable, efficient, and low-cost force protection for tactical vehicles and Soldier armor—a key military requirement for the future. The innovations and methods developed by this MURI team will provide the basis for much of the military armor for the foreseeable future.

## Abbreviations

2D	two-dimensional
3D	three-dimensional
ACM	Association for Computer Machinery
AFOSR	Air Force Office of Scientific Research
AFRL	Air Force Research Laboratory
AlGaN	aluminum gallium nitride
AlN	aluminum nitride
ANN	artificial neural network
ARL	Army Research Laboratory
ARO	Army Research Office
ASD(R&E)	Assistant Secretary of Defense for Research and Engineering
ASW	anti-submarine warfare
ATC	air traffic control
ATM	asynchronous transfer mode
Au	gold
AWACS	Airborne Warning and Control System
BEC	Bose-Einstein Condensate
BMC	Boston Micromachines Corporation
CANE	Center for Advanced Nitride Electronics
Cr	chromium
DARPA	Defense Advanced Research Projects Agency
DCPD	dicyclopentadiene
DHS	Department of Homeland Security
DNA	deoxyribonucleic acid
DoD	Department of Defense
DoDI	DoD Instruction
DPN	Dip-Pen Nanolithography
DSB	Defense Science Board
DTIC	Defense Technical Information Center
DTRA	Defense Threat Reduction Agency
EM	electromagnetic
EO	electro-optic
EPIC	electronic-photonic integrated circuits
FDA	Food and Drug Administration
FY	Fiscal Year
GaAs	gallium arsenide
GaN	gallium nitride
GDP	gross domestic product
GNOME	Global Network of Optical Magnetometers for Exotic Physics

GPS	Global Positioning System
НВТ	heterojunction bipolar transistor
HEMT	high-electron mobility transistor
HHG	high-harmonic generation
HIFU	high intensity focused ultrasound
HIV	human immunodeficiency virus
IAC	Information Analysis Center
IC	integrated circuit
ICB	Institute for Collaborative Biotechnologies
IDA	Institute for Defense Analyses
IED	improvised explosive device
IEEE	Institute of Electrical and Electronics Engineers
ILSI	International Life Sciences Institute
InAs	indium arsenide
InP	indium phosphide
IP	intellectual property
IR	infrared
ISDE	Institute for Space and Defense Electronics
ISN	Institute for Soldier Nanotechnologies
ISR	intelligence, surveillance, and reconnaissance
JPL	Jet Propulsion Laboratory
KDP	potassium dihydrogen phosphate
LANL	Los Alamos National Laboratory
	liquid crystal
LED	light-emitting diode
LIDAR	light detection and ranging
LiNbO <sub>3</sub>	lithium niobate
LLNL	Lawrence Livermore National Laboratory
MEMS	microelectromechanical systems
MIT	Massachusetts Institute of Technology
MOST	Multidisciplinary Optical Switching Technology
MOW	multiple quantum well
MRI	Magnetic Resonance Imaging
MURI	Multidisciplinary University Research Initiative
MxL	molecular transfer lithography
NAE	National Academy of Engineering
NAS	National Academy of Sciences
NASA	National Aeronautics and Space Administration
NIH	National Institutes of Health
NIST	National Institute of Standards and Technology
NRL	Naval Research Laboratory
NSP	nanosized particle
NSSEFF	National Security Science and Engineering Faculty Fellow
NSWC	Naval Surface Warfare Center
NV	nitrogen vacancy
ONR	Office of Naval Research

OSD	Office of the Secretary of Defense					
PETN	pentaerythritol tetranitrate					
PI	principal investigator					
PM	program manager					
ppb	parts per billion					
PSA	prostate-specific antigen					
PVA	polyvinyl alcohol					
QC	quantum computer					
QCSE	quantum-confined Stark effect					
QKD	Quantum Key Distribution					
QM	quantum mechanics					
R&D	research and development					
R&E	Research and Evaluation					
RF	radio frequency					
S&T	science and technology					
SAM	self-assembled material					
SBIR	Small Business Innovation Research					
SERF	spin-exchange-relaxation-free					
SiC	silicon carbide					
SME	subject matter expert					
SNA	Spherical Nucleic Acid					
STEM	science, technology, engineering, and mathematics					
TCAD	Technology Computer-Aided Design					
TDI	Transfer Devices, Inc.					
UARC	University Affiliated Research Center					
UAV	unmanned aerial vehicle					
URI	University Research Initiative					
USPTO	United States Patent and Trademark Office					
UV	ultraviolet					
VLSI	Very Large Scale Integrated					
VUV	vacuum ultraviolet					
XUV	extreme ultraviolet					
XUV	extreme ultra-violet					
μCΡ	microcontact printing					
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The Multidisciplinary University Research Initiative (MURI) Program is a multi-agency Department of Defense (DoD) effort						
that supports multidisciplinary research teams at academic institutions whose efforts intersect more than one traditional science and engineering discipline. This report reviews the achievements of the MURI program and assesses the						
scientific, economic, and military impact of a set of 25 highlighted projects that were identified as successful. A metric-						
based approach along with a qualitative analysis was used to select the 25 projects to highlight for this report from the over						
600 grants that have been awarded during the 25+ years of the MURI program. The metrics used were publications,						
with program managers and government researchers. The report provides insight into the value of funding basic research						
through the MURI program and recommendations for how to sustain a high level of performance from the program in the						
future.						
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