



AMPTIAC

QUARTERLY

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Special Issue

*DOD
Researchers
Provide*

A Look Inside Nanotechnology



One of my colleagues from the DOE made the comment a few months ago over dinner that if his proposals did not have the term “Nano/Info/Bio-Tech” in the title, there was little chance of them getting funded. We all laughed and commented on how sometimes the *buzzwords* of the moment influence our research efforts more than the warfighter, defense needs, national interests, or for that matter, intellectual curiosity. How many times have you written a proposal and carefully crafted

Editorial: Nanotechnology is More Than the Latest Engineering Buzzword

the title to utilize a word or phrase that at the time was recognized as a buzzword, just to grab a sponsor’s attention?

I am afraid we are all guilty, and in some respects, nanotechnology very effectively fits this category. You see it all over the national media, from ABC to TLC, from USA Today to the Wall Street Journal, and from Time Magazine to Scientific American. And now this special issue of the AMPTIAC Newsletter has landed on your desk, filled with information on nanotechnology. Thus, one could say that we too have fallen prey to the latest pop-culture trend of science.

Now that I have said what many of you may be thinking, let me explain why we have dedicated significant portions of the last 12 months to generating the thick, full color document you hold in your hands, and why we hope that you will come away from this with a better understanding of nanotechnology and what it means to the DOD in the 21st century.

People have worked with the nanoscale for centuries, but until recently lacked the analysis capability to understand its impact. The 20th century dramatically changed that, first with ground-breaking tools for investigating the microscale, then even more astounding tools that enabled investigation of individual atoms. Armies of engineers have driven advances in processing capabilities which have enabled first micro-, then nanotechnology to move from science fiction to engineering fact. Much like the assembly line revolutionized conventional manufacturing in the early 1900s, batch fabrication and bulk micromachining have again turned industry on its ear. The pace of these changes is increasing, with nanoprocessing already in existence and growing at an exponential rate. Some used to believe that a handful of computers would be enough to satiate the world’s needs. Others believed that sequencing the human genome would take decades, but it was finished in 15 years.

Today many people believe that molecular-level manufacturing is impractical, but there are materials and structures being produced right now that we don’t even know how to test or analyze yet.

With the help of Dr. James Murday (Superintendent of the Chemistry Division at the Naval Research Lab, and Director of the White House initiated National Nanotechnology Coordinating Office) we have recruited a stellar team of DOD researchers to explain how this field is making real contributions now, and what its potential contributions will mean to the defense of our Nation in the future. In clear, unambiguous terms, these authors have carefully laid out key aspects of the science, physics, electronics, chemistry and engineering that are advancing nanoscience at a blistering pace. From relatively simple coatings with five times the toughness and wear resistance of conventional materials, to the building blocks of optical and molecular-based computers that are generations ahead of current silicon-based machines, you will see that nanotechnology is more than the latest “flavor of the month.”

If you are a regular reader of the Newsletter, then you already know that AMPTIAC’s primary mission is to be a voice for the defense materials and processing community. We therefore provide you within these pages a snapshot of what the DOD is doing to utilize nanotechnology and nanomaterials in practical terms to improve the readiness of the warfighter. After reading this issue, you will see that today’s nanoscience is laying the foundation for the future of nanotechnology, transitioning many science-level advances to technology applications in the near and long term. Nanotechnology is more than just a buzzword; it is a natural extension of the history of engineering innovation that has brought us to this point in time. When the visions of our researchers and the promise of this field are realized, nanotechnology could very well change the foundations of engineering, manufacturing and culture.

Wade Babcock
Technical Content Manager

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Dr. James S. Murday, Executive Secretary, Nanoscale Science, Engineering and Technology Subcommittee, US National Science and Technology Council and Superintendent of the Chemistry Division, Naval Research Laboratory

At the most basic level of common understanding, nanoscience involves the study of materials where some critical property is attributable to an internal structure with at least one dimension less than 100 nanometers. This is truly the last frontier for materials science. As "nanotechnology" appears ever more often in the technical and popular media, defense researchers tackle the science and technology that will transform nanoscience into practical technology. Dr. Murday provides an overview of the efforts of the President's National Nanotechnology Initiative, its accompanying work within DOD, and what they mean to the military, our adversaries, and the future of this exciting field.

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Col. Kip Nygren, Professor and Head, Civil and Mechanical Engineering, US Military Academy

Technology is changing rapidly and often outpaces humanity's ability to comprehend its advance. We, as humans, have always relied on our superior abilities to gather and process information and make proper decisions in a timely manner. This skill spans the ages from stalking larger mammals in a hunt, to defeating our enemies on the field of battle. Now more than ever, success on the battlefield is dependent on the rapid access to information and the ability to act on that data. Changing technology presents some tremendous opportunities as well as pitfalls. Col. Nygren delves into the world of advanced technology and how it is shaping tomorrow's warfighter.

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Dr. Richard Vaia, Materials and Manufacturing Directorate, Air Force Research Laboratory

Humans place great importance on materials when talking about the past, from types of manufacturing to even more fundamental conventions of naming specific epochs after the materials used (i.e. Stone Age, Bronze Age, Iron Age). Today's frontiers of materials technology are most definitely rooted in the combination of various materials to achieve specific goals with the greatest efficiency of properties. Dr. Vaia shows us how advanced plastics and composites designed for extreme service and environments are blazing a trail for tomorrow's incredible advances.

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Dr. Richard Carlin, Director of the Mechanics and Energy Conversion Division, Office of Naval Research

Dr. Karen Swider-Lyons, Chemistry Division, Naval Research Laboratory

Probably one of the most established areas of nanotechnology is the use of nanomaterials in power generation and storage. While highly dispersed nanoscale platinum particles have been used as electrocatalysts in fuel cells for years, the use of nanomaterials in storage and generation is far from fully exploited. Each year, researchers push the envelope with advances in control and modification of nanoscale properties in electrode structures. Drs. Carlin and Swider-Lyons explain some of the most recent advances in the state of the art.

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Richard Lane, Benjamin Craig and Wade Babcock, AMPTIAC Technical Staff

May we suggest that you read this article first? Messrs. Lane, Craig and Babcock provide a comprehensive primer which introduces the science of the nanoscale. The text is written at a level any reader, from the experienced nanotechnologist to the layperson, will appreciate. Many basic aspects of the technologies described in the other articles in this issue are also explained in clear, concise terms. This is definitely a good starting point for the non-"nano-savvy" reader.

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Dr. Lawrence Kabacoff, Materials Science and Technology Division, Office of Naval Research

Most military and commercial applications require surface coatings which can resist wear and corrosion. Often taken for granted, these coatings can dramatically affect the standard service intervals for machinery, useful life of large components, and overall readiness of vital systems. While most ceramic coatings do wear very slowly, they usually fail from a lack of toughness and not a lack of wear resistance. Dr. Kabacoff describes an innovative processing method which utilizes traditional equipment to deposit films of intermixed nano- and microscale grains which stand up to wear, but provide significant improvements in toughness and durability.

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Dr. Andrzej Miziolek, Weapons and Materials Research Directorate, Army Research Laboratory

From the first experiments with gunpowder and fireworks to the latest ammonium nitrate and powdered aluminum high explosives, man has sought to unleash the force of chemical explosives in more powerful and controlled ways. Nanotechnology allows researchers to bridge the gap between pure chemical evaluation and microstructural analysis, and better understand the phenomena which make energetics work. Dr. Miziolek presents a guided tour of some of the most groundbreaking work going on today in energetics and how nanoscience is improving our understanding of one of our oldest weapons of war.

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Drs. Paul Amirtharaj, John Little, Gary Wood, Alma Wickenden and Doran Smith, Sensors and Electron Devices Directorate, Army Research Laboratory

The battlefield is a place where too much information is rarely a problem. Our soldiers need every bit of data that can be collected and the field of available sensors and sensing systems is growing every day. An elite team of ARL researchers present some of the latest thinking in sensor technology and describe how nanotechnology is changing the way sensors are designed, powered, deployed and utilized in the battlespace.

Fabricating the Next Generation of Electronics from Molecular Structures

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Dr. Christie Marrian, Microsystems Technology Office, Defense Advanced Research Projects Agency

Computers today are fabricated primarily from silicon, its oxides and nitrides, and thin films of metals, all deposited with patterning technologies that are quickly approaching a physical limit of resolution. What if the next paradigm of computing was based not on the solid, electron conducting paths of silicon and metal compounds, but on molecules and the very atomic structures that make up our own brains? Dr. Marrian takes us to the limits of molecular-based computing with healthy doses of science-fact and practical evaluation of components and systems that may very well be the next revolution in computing.

Engineering the Future of Nanophotonics

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Dr. Bob Guenther, Physics Department, Duke University

Dr. Henry Everitt, Associate Director of the Physics Division, Army Research Office

Optical components are already established as the foundation for tomorrow's telecommunications systems, and are quickly becoming de rigueur in next generation computing technology. In order for this to move from the world of science to technological application, new ways of controlling, transmitting and conveying photonic information will be developed. Drs. Guenther and Everitt examine the world of nanophotonics and show some of the systems that will transmit, generate, and indeed compute with light.

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The Coming Revolution

Science and Technology of Nanoscale Structures

Dr. James S. Murday
 Superintendent, Chemistry Division, Naval Research Laboratory
 Executive Secretary, National Science and Technology Council's Subcommittee on Nanoscale Science, Engineering and Technology

Introduction

The term "Nanoscience" is appearing in the technical literature at an increasing frequency and each reference offers its own definition, some of which are better than others. At the most basic level of common understanding, nanoscience involves materials where some critical property is attributable to an internal structure with at least one dimension limited to between 1 – 100 nanometers. Below that size, the disciplines of chemistry and atomic/molecular physics have already provided detailed scientific understanding. Above that size scale, the last 50 years of condensed matter physics and materials science have provided a detailed scientific understanding of microstructures. So, in some respects, one might consider the nanoscale to be the last "size" frontier for materials science.

The interest in nanostructures extends beyond their individual properties. We have learned to exploit the natural self-assembly of atoms/molecules into crystals. The directed self-assembly of nanostructures (one, two and three dimensioned) into more complex, hierarchical systems is also an important

Figure 2. Superlattice Devices Formed through One-Dimensional Nano-Technology Processing



NRL InAs/AlSb HEMT

High Electron Mobility Transistor (HEMT)
 High frequency receiver/transmitter receiver

Quantum Cascade (QC) Laser Gas Sensor



Lucent Technologies

Vertical Cavity Surface Emitting Laser (VCSEL)
 Fiberoptic data communications, optical sensors, encoder, range finder



Honeywell VCSEL

Figure 1. Paleontology of Nanostructures

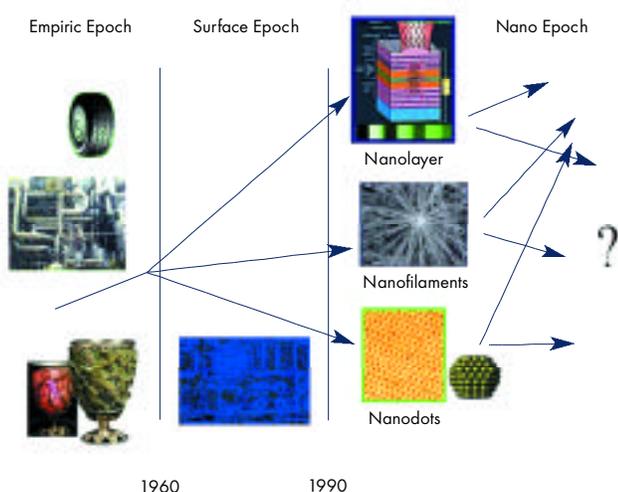


Figure 3. Nanoscience Literature Citation Counts

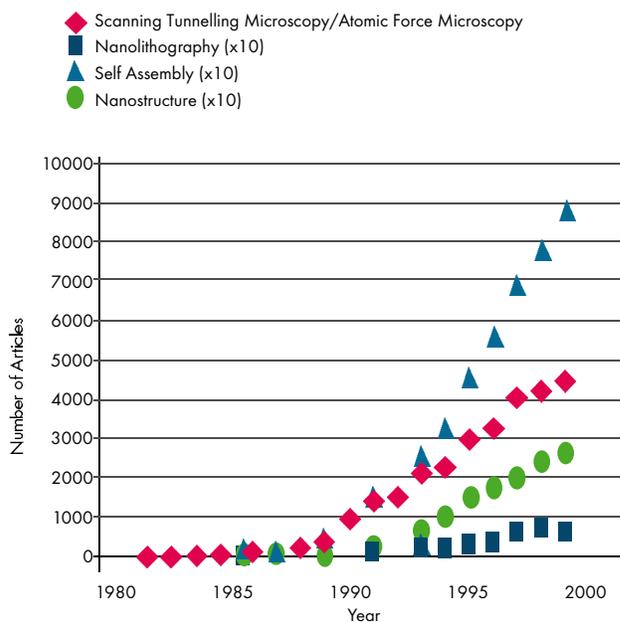


Table 1. Carbon Nanotubes: Prediction and Subsequent Confirmation

Prediction	Experimental Confirmation
<ul style="list-style-type: none"> Armchair single wall nanotubes (SWNT) metallic Mintmire, Dunlap, White, Phys. Rev. Let. 68, 631 (1992) 	<ul style="list-style-type: none"> Individual single-wall carbon nanotubes as quantum wires Tans, et al. Nature 386, 474 (1997)
<ul style="list-style-type: none"> All metallic SWNTs have a linear dispersion relation $e(k)$ near the Fermi level with a slope in k vs. e of $-1.88 \text{ nm}^{-1} \text{ eV}^{-1}$ Mintmire, Dunlap, White, Phys. Rev. Let. 68, 631 (1992) 	<ul style="list-style-type: none"> Two-dimensional imaging of electronic wavefunctions in carbon nanotubes Lemay, et al. Nature 412, 617 (2001)
<ul style="list-style-type: none"> Elastic modulus should be similar to high stiffness in-plane modulus of graphite, Robertson, Brenner, Mintmire, Phys. Rev. B. 45, 12592 (1992) 	<ul style="list-style-type: none"> Nanobeam Mechanics: Elasticity, Strength, and Toughness of Nanorods and Nanotubes, Wong, Sheehan, and Lieber, Science 277, 1971 (1997)
<ul style="list-style-type: none"> Bandgaps of semiconducting SWNTs should obey an analytic relationship inversely proportional to SWNT diameter White, Robertson, Mintmire, Phys. Rev. B. 47, 5485 (1993) 	<ul style="list-style-type: none"> Atomic structure and electronic structure of single-walled carbon nanotubes Odom, Huang, Kim, and Lieber, Nature 391, 62 (1998)
<ul style="list-style-type: none"> Bandgaps of quasi-metallic SWNTs are inversely proportional to the square of the SWNT diameter, White, Robertson, Mintmire, Clusters and Nanostructured Materials, (Nova, NY 1996) p. 231 	<ul style="list-style-type: none"> Energy gaps in metallic single-walled carbon nanotubes Ouyang, Huang, Cheung, Lieber, Science 292, 702 (2001)
<ul style="list-style-type: none"> Stability of metallic SWNT conduction channels in presence of disorder, leading to exceptional ballistic transport properties White, Todorov, Nature 393, 240 (1998) 	<ul style="list-style-type: none"> Recent Confirmation: Fabry-Perot interference in a nanotube electron waveguide Liang et al., Nature 411, 665 (2001)
<ul style="list-style-type: none"> Near the Fermi level all semiconducting (metallic) SWNTs with similar diameters will have similar densities of states with the positions of the first few peaks obeying a simple analytic relation, White, Mintmire, Nature 394, 29 (1998) 	<ul style="list-style-type: none"> Spatially resolved scanning tunneling spectroscopy of single-walled carbon nanotubes, Venema et al., Phys. Rev. B. 62, 5238 (2000)

Table 2. Characteristic Lengths In Solid State Science Model

Field	Property	Scale Length
Electronic	Electronic Wavelength	10 – 100nm
	Inelastic Mean Free Path	1 – 100nm
	Tunneling	1 – 10nm
Magnetic	Domain Wall	10 – 100nm
	Exchange Energy	0.1 – 1nm
	Spin-Flip Scattering Length	1 – 100nm
Optic	Quantum Well	1 – 100nm
	Evanescient Wave Decay Length	10 – 100nm
	Metallic Skin Depth	10 – 100nm
Superconductivity	Cooper Pair Coherence Length	0.1 – 100nm
	Meisner Penetration Depth	1 – 100nm
Mechanics	Dislocation Interaction	1 – 1000nm
	Grain Boundaries	1 – 10nm
Nucleation/Growth	Defect	0.1 – 10nm
	Surface Corrugation	1 – 10nm
Catalysis	Localized Bonding Orbitals	0.01 – 0.1nm
	Surface Topology	1 – 10nm
Supramolecules	Primary Structure	0.1 – 1nm
	Secondary Structure	1 – 10nm
	Tertiary Structure	10 – 1000nm
Immunology	Molecular Recognition	1 – 10nm

goal. Without direct self-assembly, manufacturing costs would severely limit the impact of nanotechnology.

While a scientific understanding of nanostructures is incomplete, their use in technology dates back at least two thousand years. The Lycurgis cup, a Roman artifact pictured in the lower left of Figure 1, utilized nanosized gold clusters to provide different colors depending on front or back lighting. The Roman artisans knew how to achieve the effect, but were unaware of its

nanocluster basis. In the 20th century, nanostructures contributed to *many* significant technologies. Examples of these include the addition of nanosized carbon particles to rubber for improved mechanical properties (tires), the use of nanosized particles for catalysis in the petrochemical industries, and the nucleation of nanosized silver clusters during photographic film exposure. As depicted in Figure 1, one might assign these examples to an empiric epoch in the continuing evolution of nanotechnology.

Empirically-based technology, without greater scientific understanding, is usually difficult to extend or control. The scientific foundation of nanostructures received a quantum advance when surface science enjoyed a renaissance, starting in the 1960s. Surface science constrained one material dimension into the nanometer size scale. Events catalyzing that renaissance were the development of new surface-sensitive analytical tools, the ready availability of ultra-high vacuum (a by-product of the space

race), and the maturity of solid-state physics (surfaces representing a controlled lattice defect – termination of repeating unit cells). The principal economic driving force was the electronics industry, but surfaces were also recognized to play an essential role in many “reliabilities” – adhesives, corrosion protection, friction, wear, fracture, etc. From 1960 to the present, surface science has progressed from “clean, flat and cold” into thin films (two or more nanoscale interfaces) and film process-

ing. Surface science has provided the scientific underpinning that enabled a key aspect of “Moore’s Law” – the rapid miniaturization of thin film electronics technologies. Superlattice devices (see Figure 2) are a manifestation of the rapidly growing technology, where the individual layers are nanometers in thickness and the interfaces are controlled with atomic precision.

So, if nanotechnology has been around so long, why is it only now the current rage? The 1990s nanoscience renaissance has close parallels to the 1960 surface science renaissance. First, beginning in 1980, the discovery and development of proximal probes, such as scanning tunneling microscopy/spectroscopy, atomic force microscopy/spectroscopy, and near-field microscopy/spectroscopy have all provided tools for measurement and manipulation of individual nanosized structures. It took 10-15 years for reliable commercial instruments to come onto the market which then led to a rapid increase in refereed nanoscience publications beginning in the early 1990s. Figure 3 highlights these increases for several subject areas. The properties of individual nanostructures can now be observed, rather than relying on ensemble-averaged values. In turn, those properties can be defined in terms of composition and/or structures, and with such an understanding comes the possibility for control.

Second, in addition to the new experimental measurement capabilities, computer technology is now sufficiently advanced (speed and memory capacity) such that accurate predictions, even based on first principles (see *AMPTIAC* newsletter Vol. 5, #2, page 1), are enabled for the number of atoms incorporated in a nanostructure (see Table 1). Analytic predictions, made years before experimental measurements could confirm their

validity, are now being proven true by direct experimentation. There is no doubt that modeling and simulation will play a leading role in the nanotechnology race.

Third, the disciplines of biology, chemistry, materials, and physics have all reached a point where nanostructures are of interest – chemistry building up from simpler molecules, physics/materials working down from microstructures, and biology sorting out from very complex systems into simpler subsystems. If one expected to simply extrapolate the properties of nanostructures from the size scales above or below, then there would be little reason for the current interest in nanoscience or nanotechnology.

There are three reasons why nanostructured materials behave very differently than their adjacent scales. 1) Large surface-to-volume or interface-to-volume ratios, 2) size effects (where cooperative phenomena like ferromagnetism are compromised by the limited number of atoms/molecules), and 3) quantum effects. Many of the models for materials properties at the micron and larger sizes have characteristic length scales of nanometers (see Table 2). When the size of the structure is in the nanometer range, those parameters are no longer adequate to model/predict the property. As such, one can expect “surprises,” resulting in new materials behavior that may be technologically exploitable.

Finally, there are several economic engines driving the interest in nanotechnology, with information technology (electronics), biotechnology (pharmaceuticals and healthcare), and materials being the most likely beneficiaries (see Table 3).

With these substantial scientific and economic opportunities, it’s not surprising to find strong global interest in fostering nanoscience, with the intent of accelerating scientific discovery into innovative commercial products. Table 4 compares estimated governmental funding in nanosciences around the globe. From estimates of FY02 budgets, it is anticipated that over \$1.5B will be invested in nanoscale science and technology (S&T) in 2002. Care should be taken when comparing

Table 3. Potential Global Economic Impact of Nanotechnology in 15-20 Years [1]

Materials; Materials Processing	\$340B
Information Technology Devices	\$300B
Pharmaceuticals/Biotechnology	\$180B
Chemical Manufacturing, Catalysis	\$100B
Aerospace	\$70B
Tools, Automation, Life Cycle Costs	\$20B
Healthcare - Diagnostics, Prosthetics	\$30B
Sustainability - Agriculture, Water, Energy	\$45B
Total	~\$1T

Table 4. “Nanotechnology” Research Program Investment (\$M)

	1997	2000	2001	2002
USA	115	270	420	600
Japan	120	245	500	900
Western Europe	125	200	250	300
Other Countries (FSU, China, Australia, others)	70	110	200	400
Total	430	825	1,400	>2,200

Table 5. US National Nanotechnology Initiative Program (\$M) (Funding Breakdown)

Category	Lead	FY00	FY01	FY02
“Fundamental” Research		87	140	*
Grand Challenges		71	125	*
Nanostructured Materials by Design	NSF			
Nanoelectronics, Optoelectronics, Magnetics	DOD			
Advanced Healthcare/Therapeutics	NIH			
Environmental Improvements	EPA			
Energy Conversion/Storage	DOE			
Transportation	DOT			
Microcraft and Robotics	NASA			
Instrumentation & Metrology	NIST			new
Manufacturing Science	NSF			new
CBRE Protection/Detection	DOD			new
Centers/Networks		47	66	*
Infrastructure		50	77	*
Ethical/Social Implications		15	21	*
Totals (est.)		270	429	600

* Figures not available at press

Table 6. Nanotechnology Centers

Center Title	Investigator	Institution
National Science Foundation		
Nanoscale Systems in Information Technologies	Buhrman	Cornell
Center for Nanoscience in Biological & Environmental Engineering	Smalley	Rice
Nanoscale S&E Center for Integrated Nanopatterning & Detection	Mirkin	Northwestern
Center for Electronic Transport in Molecular Nanostructures	Yardley	Columbia
Nanoscale Systems and their Device Applications	Westervelt	Harvard
Center for Directed Assembly of Nanostructures	Siegel	RPI
DOE		
Integrated NanoSystems	Michalske	Sandia/Los Alamos
Nanostructured Materials	Lowndes	Oak Ridge
Molecular Foundry	Alivisatos	Lawrence Berkeley
NASA		
Bio/Nano/Information Technology Fusion		TBD in 02
Bio-Nanotechnology Materials and Structures for Aerospace Vehicles		TBD in 02
Nanoelectronics Computing and Electronics		TBD in 02
DOD		
Institute for Soldier Nanotechnologies		TBD in 02

funding levels between different countries. For instance, one estimate of nanotechnology investment in China is around \$25M/year; however, the manpower costs in China are significantly less than in the US, therefore, their investment is not as small as it might otherwise seem.

US National Nanotechnology Initiative

The US response to the nanoscale scientific and economic opportunities is the National Nanotechnology Initiative (NNI) [2]. The funding categories for the NNI are provided in the National Nanotechnology Initiative supplement to the President's FY2001 Budget [3]. The annual investment levels in nanoscience are presented in Table 5. It would be fair to say that all of the S&T funded under the NNI is fundamental research. On the other hand, the S&T activity designated as "fundamental" in Table 5 corresponds to NSF investment where the principal motivation is the generic knowledge base and education.

In the 'Grand Challenges' section of Table 5, the fundamental research investments listed are selected with technological ramifications in mind. The lead agency has the responsibility for surveying the investment in the designated Grand Challenge and for identifying investment opportunities/shortfalls. There are three new grand challenges in FY02; the last, 'Chemical/Biological/Radiological/Explosive (CBRE) for Detection/Protection', seeks to enable the considerable opportunities for nanostructures to impact homeland defense. As with any rapidly changing technology, there is some anxiety over potential economic, environmental and social disruption by nanotechnology. In response, NSF has sponsored a workshop to address these issues [4].

It is expected that nanoscience/nanotechnology will enable many important advances at the boundaries between traditional disciplines. Interdisciplinary research must be fostered to accelerate that expectation. Cutting edge research will also require expensive instrumentation for measurement and manipulation of nanostructures. The Centers/Networks and

Infrastructure categories are meant to address these two points. Table 6 shows new Centers initiated under the NNI. The DOE Centers will be user facilities available to all scientists/engineers in a way similar to the DOE synchrotron radiation facilities.

The NNI focuses on nanoscience as the enabler of nanotechnology. Experience has shown that it takes 10-20 years for a scientific discovery to lead to a commercial product. However, among the surface science-stimulated technologies, there are a number of products now entering the market. These products are mostly the nano-

dots and nanowires that are the building blocks for systems, but there are also composite materials. A representative listing of those products is shown in Table 7.

DOD Contributions to the NNI

The DOD has been investing in fundamental nanoscience research for over 20 years. One of the early programs dating back to the 1980s was Ultra-submicron Electronics Research (USER). In 1997, the DOD identified several S&T topics with the potential for significant impact on military technology. Nanoscience was selected as one of several special research area (SRA) topics. A website [5] and coordinating committee were established. Its current membership is comprised of Drs. Gernot Pomrenke (Air Force), John Pazik (Navy), Bob Guenther (Army), and Christie Marrian (DARPA). Further, each Service has a coordinating group to guide its nanoscience program (see Table 8). There are many potential areas where nanoscience/nanotechnology may significantly impact DOD missions. A selected listing is provided in Table 9.

Each Service has its own laboratory nanoscience programs (see www.nanosra.nrl.navy.mil). The Army efforts in nanoelectronics, nanooptics, organic light emitting diodes (OLEDs) and displays, sensors, and NanoElectromechanical Systems (NEMS) are centered at ARL Adelphi; the work on organic nanomaterials is largely at ARL Aberdeen. The Air Force nanomaterials program is largely centered at Wright Patterson AFB in Dayton. This work is focusing on nanocomposites, inorganic nanoclusters, nanophase metals and ceramics, nanotribology, nanobiomimetics and nanoelectronics. The Navy program is centered at the Naval Research Laboratory in Washington, DC. NRL has just created a Nanoscience Institute with the goal of fostering interdisciplinary research that cuts across the NRL organizational structures (<http://nanoscience.nrl.navy.mil/>). A new Nanoscience Building at NRL has been specially designed to minimize those noise sources that would limit measurement and manipulation precision. The new building will open in 2003 (see Table 10). NRL is interested in collaborative projects

Table 7. Examples of Commercially Available Nanotechnology Products**Nanopowders**

Altair	www.altairtechnologies.com/	TiO ₂
Argonide Nanomaterials	www.argonide.com	aluminum
Bosch	www.bosch.de	ceramics
BuckyUSA	www.flash.net/~buckyusa/	fullerenes
Inframot Corporation	www.inframot.com	Yttria Stabilized Zirconia (YSZ), FeS, n-WC/Co, Co/SiO ₂ , Ni-Fe/SiO ₂
Nanomaterials Research Corp	www.nrcorp.com	oxides
Nanophase Technologies	www.nanophase.com	oxides
Nanopowder Enterprises	www.nanopowderenterprises.com/	oxides, metals
NanoPowder Industries	www.nanopowders.com/	precious/base metals
Nanox	www.nanox-online.com/	ZnO
NexTech Materials	www.nextechmaterials.com/	oxides
Plasmachem	www.plasmachem.de	diamond, alumina, SiC, Cu
US Nanocorp, Inc	www.usnanocorp.com	n-MnO ₂ , n-Ni(OH) ₂ , n-FeS ₂
Powdermet	www.powdermetinc.com/	metals, ceramics
Nanomat Ltd (Ireland)	www.nanomatgroup.com/	metal oxides

Nanowires/Nanotubes

Carbon Solutions (Sweden)	www.carbonsolutions.se/	carbon nanotubes (CNT)
Carbolex	www.carbolex.com	single wall nanotube (SWNT)
Carbon Nanotechnology	www.cnanotech.com/	SWNT
Hyperion Catalysis	www.fibrils.com/	multiwalled nanotubes (MWNT)
Materials & Electrochem. Res.	www.mercorp.com/	SWNT, MWNT
NanoLab	www.nano-lab.com/	CNT and arrays
Sun Nanotech (China)	www.sunnano.com/	MWNT
Piezomax	www.piezomax.com/	Carbon Nanotube SPM Tips
eSpin	www.nanospin.com/	polymer nanofibers

Nanocomposites

Inframot	www.inframot.com/	magnetic nanocomposite
Nanocor	www.nanocor.com/	clay in plastics
RTP	www.rtpcompany.com/	CNT compounds
Southern Clay Products	www.nanoclay.com/	clay in plastics
Triton Systems Inc	www.tritonsys.com/	nanoparticles in plastics
Hybrid Plastics	www.hybridplastics.com/	organic/inorganic hybrids

with other Services that can exploit this new building and its specialized nanoscience measurement/manipulation equipment.

Since some of the DOD nanoscience programs are nearly 20 years old, one might expect transition successes. One example from each service is illustrated here.

Under Army funding Dr. Chad Mirkin, Northwestern University, invented a way to utilize nanoclusters of gold for the sensitive, selective detection of DNA. This technology has been demonstrated to work for anthrax. It is now being commercialized by the start-up firm Nanosphere, and is presently under clinical evaluation.

The Air Force funded Triton Technologies Inc. under the SBIR program to insert nanostructured clay particles into polymers. One benefit of this composite is reduced gas permeability. This new material was marketed by Converse in athletic shoe heels with greater elasticity (He gas bubbles trapped by the low permeability polymer composite). The reduced permeability is also of interest to the Army for packages containing food, beverages and pharmaceuticals. The Navy is interested because nanoclay particles increase the fire resistance of organic composite materials.

Table 8. DOD Points of Contact on Nanotechnology**Navy Nanostructures Working Group**

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Dr. Gary Hagnauer	Weapons and Materials, ARL	(ghagnau@arl.army.mil)
Dr. Raju Namburu	Computation and Information, ARL	(raju@arl.army.mil)

Table 9. Nanoscale Opportunities with Major DOD Impact**Nanoelectronics/Optoelectronics/Magnetics**

Network Centric Warfare
Information Warfare
Unmanned Combat Vehicles
Automation/Robotics for Reduced Manning
Effective Training Through Virtual Reality
Digital Signal Processing and Low Probability of Intercept

Nanomaterials "by Design"

High Performance, Affordable Materials
Multifunction Adaptive (Smart) Materials
Nanoengineered Functional Materials (Metamaterials)
Reduced Maintenance (halt nanoscale failure initiation)

BioNanotechnology – Warfighter Protection

Chemical/Biological Agent detection/destruction
Human Performance/Health Monitor/Prophylaxis

Table 10. NRL Nanoscience Building Requirements**Class 100 Cleanroom – 5,000 sq ft, ballroom style**

Chemical (hoods, wet processing stations,...)
 Dry Processing (dual focused ion beam, chemical vapor deposition,...)
 Photolithography (pattern aligner,...)
 Nanolithography (e-beam writer, dip-pen lithography,...)

Quiet Laboratories – 8 @ 400 sq ft

EMI <0.3 mG pp 60 Hz
 Vibration <3 μ m/sec rms 10-100 Hz
 Acoustic <35dB @ 1kHz
 Temperature \pm 0.5 °C, <0.5 °C/hr
 Humidity 45 \pm 5%

Ultraquiet Laboratories – 4 @ 400 sq ft

EMI <0.3 mG pp 60 Hz
 Vibration <3 μ m/sec rms 10-100 Hz
 Acoustic <25dB @ 1kHz
 Temperature \pm 0.1 °C, <0.1 °C/hr
 Humidity 45 \pm 5%

Under Navy funding, Inframat has developed a thermally sprayed coating of alumina/titania nanopowders. The properties of this coating are far superior to the micropowder equivalent (see Table 11). This product was one of the R&D Magazine selections as an R&D 100 product of the year for 2000 and it currently under field evaluation on Naval ships.

Conclusion

DOD programs in nanoscience are major contributors to the NNI. The other articles in this issue present some of those programs and provide an assessment of the present state-of-the-art in nanoscience/nanotechnology, with particular emphasis on DOD needs. There is clearly growing global interest in nanoscience and nanotechnology, driven by the science opportunities and the expectation of large economic benefits. Since the US will not dominate the advances in nanoscience and nanotechnology, it is incumbent on the DOD to invest in those nanoscience/nanotechnology areas important to its interests, to expeditiously convert nanoscience discovery into innovative Defense technologies (thereby maintaining technology superiority over opposition forces), and to pay close attention to developments outside the US.



Dr. James S. Murday received a B.S. in Physics from Case Western Reserve in 1964, and a Ph.D. in Solid State Physics from Cornell in 1970. He joined the Naval Research Laboratory (NRL) in 1970, led the Surface Chemistry effort from 1975-1987, and has been Superintendent of its Chemistry Division since 1988. From May to August 1997 he served as Acting Director of Research for the Department of Defense, Research and Engineering. He is a member of the American Physical Society, the American Chemical Society and the Materials Research Society; and a fellow of the American Vacuum Society (AVS), and the UK Institute of Physics. For the AVS, he has served as trustee for 1981-1984, director for 1986-1988, representative to the American Institute of Physics Governing Board 1986-1992, president for 1991-93, and representative to the Federation of Materials Societies 1998-present. His research interest in nanoscience began in 1983 as an Office of Naval Research program officer and continues through the NRL Nanoscience Institute. He has organized numerous International STM/NANO conferences and their proceedings. Under his direction, both the AVS and the International Union for Vacuum Science, Technology and Applications created a Nanometer Science/Technology Division. He is Executive Secretary to the US National Science and Technology Council's Subcommittee on Nanoscale Science Engineering and Technology (NSET) and Director, National Nanotechnology Coordination Office.

Table 11. Properties of Inframat Nanoalumina/Titania Coating (www.inframat.com)

Properties	Conventional Alumina/Titania	Nanostructured Alumina/Titania	Improvement
Toughness	Poor	Excellent	Dramatic
Hardness (VHN)	1,000 VHN	1,000	-
Wear resistance (N*m/mm ³)	7.5 x 10 ³	40 x 10 ³	~5X
Corrosion Resistance	Good	Exceptional	Significant
Grindability	Poor	Excellent	Dramatic
Fatigue Life	Failure @ <1 million cycles	No failure up to 10 million cycles	>10X
Flex Tolerance	Will result in coating spallation	Can be bent to over 180 without any spallation	Dramatic
Bond Strength (psi)	1,900	~8,000	>4X

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Emerging Technologies and the Army

Col. Kip Nygren
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Most of the articles in this special issue of the Newsletter address definitions, functions, and applications of nanotechnology and nano-engineered materials. Colonel Nygren takes a broader brushstroke, providing us with a greater perspective on the rapidly changing world of high technology, and what role nanotechnology will play in the decades to come. An insightful and provocative look into the first half of the 21st Century! – Editor

The last decade of the 20th Century provided a glimpse of the speed and magnitude of the revolutionary changes that will profoundly transform society and the Army in the early part of the 21st Century. The emerging technologies that will be the major contributors to this transformation are biotechnology, nanotechnology and robotics/artificial intelligence (AI). This article considers how these technological innovations could substantially change the nature of warfare and more importantly, highlight the Army's need to overhaul its processes and organization to cope with the acceleration of technological change.

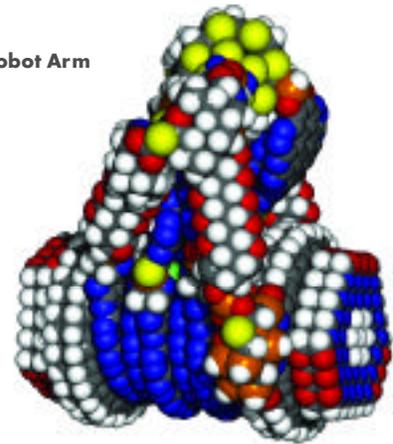
Emerging Technologies

Revolutionary technological change is coming, and two things will be different about this change than changes in the past – its magnitude and speed. The magnitude of change is going to be significantly greater than we can presently envision. There is broad agreement among experts about the general direction of technology's evolution, and that the three emerging technologies of biotechnology, nanotechnology, and robotics/AI are driving the change. The information technology innovations of the 1990's will look tame when compared to the technological revolution that will occur during the first decade of the 21st Century, wrought by the synergism of these three technologies.

BIO-ENGINEERING The sequencing of the human genome and the genomes of other species have provided access to the blueprints for the construction of biological entities and we are at the early stages of learning how to make desired modifications to those entities. This knowledge paves the way for individualized drug therapies, noninvasive surgery, tissue and organ engineering, neural and sensory implants, biological computing and countless other currently inconceivable possibilities. It is clear that the quality and length of human life will be significantly increased, and that the promise of improvements beyond current levels in all areas of human performance is within reach [1].

NANOENGINEERING In 1986, K. Eric Drexler published a book called the "Engines of Creation," [2] which revealed his

Figure 1. Nanoscale Robot Arm
(Drexler, NASA Ames)



vision of a practically utopian future that will be realized by means of revolutionary machines and structures built on the molecular scale. The size of these machines is measured in nanometers (billionths of a meter) and they would theoretically be able to manufacture any physical item, assembling it molecule by molecule from the inside out. The objects produced would be physically perfect because each and every molecule would be placed in exactly the right position. The molecular building materials would be obtained through the actions of disassemblers, taking apart source materials molecule by molecule for the assemblers to use in construction. No materials would be wasted and, therefore, pollution would be kept to an absolute minimum.

The construction of a complex device would require the assemblers to first replicate themselves to achieve a level of critical mass permitting complete fabrication of any desired part within a reasonable period of time [3]. Figure 1 is a visualization of a nanoscale robot arm intended to move atoms in the assembly process. The dream of molecular nanotechnology is to do for the atom what information technology has done for the bit [4]. This is the long-term, optimistic vision for nanotechnology, but even today methods of building nanoscale structures and machines are achieving some interesting and useful results by building from the top down. A crystal is an example of the natural growth of self-organizing nanoscale atomic structures, and similar properties are being exploited by researchers to produce a variety of nanostructures including electrical,

“We will experience an equivalent level of technological change in the first decade of the 21st Century to what we experienced in all of the 20th Century.”

mechanical, electromechanical and quantum devices [5]. Potential capabilities include the proliferation of sensors and actuators which could lead to “. . . clothes that respond to the weather, interface with information systems, monitor vital signs, deliver medicines, and automatically protect wounds; airfoils that respond to airflow; buildings that adjust to the weather;” and “bridges and roads that sense and repair cracks; . . .” [6].

Microelectromechanical systems or MEMS, measured in millionths of a meter, are currently used in a variety of applications, including the actuation of automobile airbags, fiber optic data switching, and the direct integration of analog and digital circuits on silicon chips used in cellular telephones. As published recently in *Physics Today*, “. . . the field of micromechanics will change the paradigm of what machines are, how and where we use them, what they cost, and how we design them. It may not be an exaggeration to say that we are on the verge of a new industrial revolution driven by a new and completely different class of machines” [7]. While larger than nanoscale, MEMS devices are still quite small. A MEMS-scale gear is compared to red blood cells and a grain of pollen in Figure 2.

ROBOTICS/ARTIFICIAL INTELLIGENCE The steady shrinkage of electronic components will persist into an era of nanoelectronics and permit the processing power of computers to increase well beyond that of the human brain. Computers already indirectly augment the processing capability of humans today, such as when a word processing program helps to correct a writer’s spelling errors. For many years, technology has provided replacements for bones and joints, augmentation for sight and hearing, and the support and replacement of damaged organs.

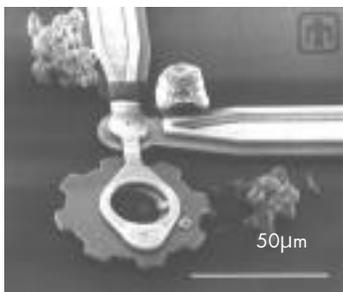


Figure 2. Micro Gear with Pollen and Red Blood Cells (Sandia National Labs)

Augmentation of human memory and mental processing through direct connection to computers will simply be a natural progression of these existing trends [8]. Extreme miniaturization will enable people and machines to interact in ways that are unimaginable except in science fiction novels.

SYNERGISTIC COMBINATIONS As these technological advances combine synergistically, they have the potential to positively and profoundly transform the world. Nanoscale intelligent robots could augment and repair living cells leading to the extension of life and enhanced individual human performance. Within 25 years, computers with a processing capability millions of times that of today’s computers will be capable of learning on their own [9]. The insights and knowledge they may learn from reading the entire expanse of human knowledge are bound to have momentous influences on our connections to and control of our environment.

Currently, bacteria are being designed by deliberate modification of their DNA to produce protein molecules for computer memory. Laboratories at the University of Connecticut and Syracuse University have designed and produced three dimensional, gigabit scale memory modules for the Air Force consisting of protein molecules suspended within a solid polymer matrix that can store electrons produced by photons of a particular wavelength and release them on demand [10]. A similar three dimensional memory medium has also been created using molecular electronics [11]. These memories can store information in a three dimensional array that is unaffected by electromagnetic impulses and extreme accelerations.

Exponential Change

Why is this great change going to occur at such a rapid rate? Studies of technological change over the past century lead to the conclusion that technology is evolving exponentially. This is not surprising since all evolutionary change is exponential, but what is surprising is the greater than expected rate of exponential technological change. Figures 3 and 4 show that manufacturing productivity and per capita GDP have increased in approximately an exponential manner over the past several years. A study of overall technological change by Raymond Kurzweil indicates that technology is advancing at approximately a seven percent rate of increase per year, or to put it another way, the effectiveness of technology doubled every ten years in the twentieth century [12].

In the first half of the last century, technology evolved over five doubling periods to become 32 times more advanced (or more complex, or more important in the life of humans) in 1950 than it was in 1900. Now, continue the doubling of progress every ten years during the later half of the century and by the year 2000, technology had become about 1000 times

more advanced, or important in our lives, than in 1900. Astonishingly, half of this change occurred in the last decade of the century and it was certainly the 1990's that brought the idea of rapid technological change to the attention of most observers. It is the nature of exponential change to materialize faster than we expect it to, because humans tend to be linear thinkers.

IMPLICATIONS FOR THE FUTURE By 2010, technology will be 2000 times more advanced than in 1900. Therefore, we will experience an equivalent level of technological change in the first decade of the 21st Century to what we experienced in all of the 20th Century! Extrapolating to the end of the 21st Century, one finds technology will have progressed to become a million times more advanced than the technology that existed in 1900. In other words, we will experience a thousand times the technological progress achieved in the 20th Century, during the 21st Century.

But what about such technologies as cars, airplanes, bicycles, the can opener, the mouse trap and many others that have not appeared to advance much at all over the last few years, much less exponentially? The history of technological advance is the story of countless different technologies erupting exponentially onto the scene and then leveling off in their growth or improvement in what is classically known as an S curve of growth. It is the summation of all technologies that is considered here and that summation presents a global image of accelerating change. This aggregate of technological change is probably best captured by such indices as manufacturing productivity and per capita GDP. These indicators are effectively exponential in nature and therefore, provide strong support to the premise that exponential change is a compelling model for understanding the accelerating advance of technology.

Implications for the Army

Although the effects of emerging technologies on the future Army cannot be known, we will speculate about some real possibilities for the future.

Figure 3. Manufacturing Productivity (US Dept of Commerce)

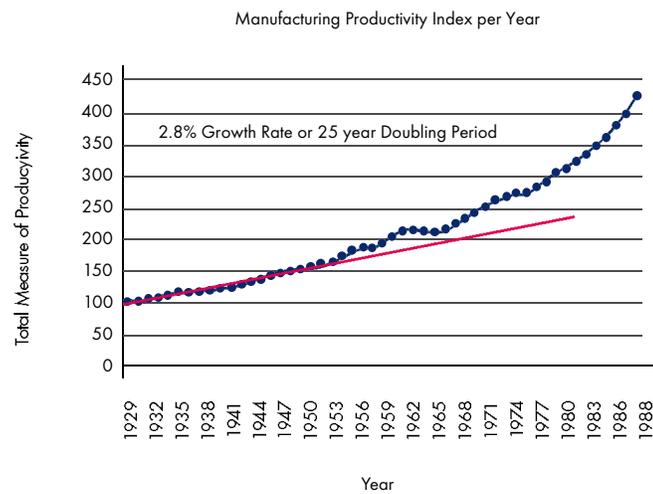
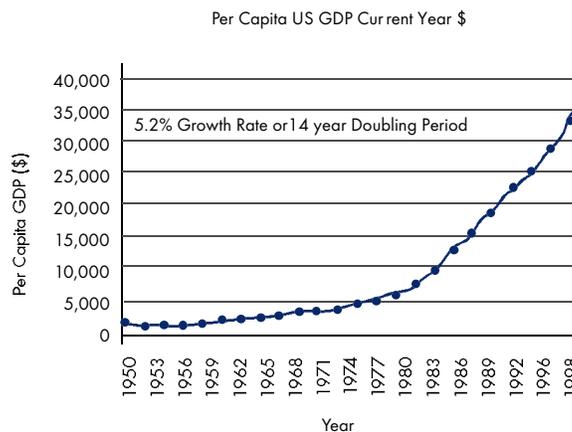


Figure 4. US Per Capita GDP Change (US Dept of Commerce)



THE DECISION CYCLE Consider the potential to augment the especially stressful and demanding decision-making process that is at the heart of winning battles and wars. An effective model of this process was developed by Colonel John Boyd of the Air Force from his observations of air to air combat in Korea. It is known as the Observation – Orientation – Decision – Act or O-O-D-A cycle. Observe - what is out there? Orient - what does that mean to me and what are my options? Decide - select the best course of action. Act - execute the course of action and begin the process over again [13]. Consider some of the ways this cycle can be enhanced by the emerging technologies under discussion, and specifically with the AI tool *Commander's Associate*.

OBSERVE – *Sense*. The Army is already using autonomous robotic vehicles as observers in Afghanistan and these will only become more reliable and effective as they are employed in the air, on the ground, and even under the ground. The miniaturization of machines, structures and electronics will make available large masses of sensors of varied types that can be deployed over the entire battle area to continuously monitor all potential enemy signatures. Automatic target recognition will relieve

either electronically or physically by autonomous air or ground vehicles.

ACT – *Make it happen*. Most importantly, the AI assistant can monitor all aspects of the action in real time and make recommendations to modify any phases of the plan as it is executed. The entire decision cycle could be completed in minutes or even seconds, as the commander desires, and can be continuously iterated by the AI to account for new data.

“The Commander’s Associate will be instrumental in assuring cycle time is less than an opponent’s ... driving the opponent to inevitably take action based on an observation that no longer applies.”

Boyd demonstrated that the cycle time is the critical factor in determining success in combat. The *Commander’s Associate* will be instrumental in assuring the friendly decision cycle time is less than an opponent’s cycle time, therefore,

some of the data processing burden and other capabilities may include the obstruction and confusion of enemy attempts to observe the telltale signatures of friendly forces.

driving the opponent to inevitably take action based on an observation that no longer applies. This will rapidly lead an enemy commander to realize that he cannot influence the situation in any coherent manner, and with any luck, in total frustration he will lose the resolve to continue the conflict.

ORIENT - *Process the Information*. The principal criticism heard about information technology in the Army is that commanders and staffs cannot adequately process the vast quantity of information available in a timely manner, resulting in more confusion and less clarity. An AI tool known as the *Commander’s Associate* will soon be available to alleviate this situation. This artificially intelligent assistant will assess and assimilate all the incoming data, draw tentative conclusions in collaboration with the commander and staff, and visually display the important information on a map or in any other desired format. All this processing is accomplished nearly instantaneously and will be continuously updated.

Weapon systems needed to create the violence, or the threat of violence in combat, will change dramatically as a result of emerging technologies. If we continue with the same basic weapon types as today, then molecular manufacturing should be able to produce these weapons, equipment and structures with minimum weight and maximum strength. Artificially intelligent and autonomous air, land and subterranean combat robots in a wide range of sizes from nanometer to meter scales will be employed individually and in swarms in conjunction with soldiers to accomplish the mission.

Because the *Commander’s Associate* also knows all the friendly forces and dispositions, it can just as rapidly offer recommended courses of action. The commander will verbally interact with the AI associate to modify and consider a wide range of feasible alternatives to accomplish the mission. By means of sensitivity analysis, the AI associate will be able to assess the impact of assumptions, advise which operational phases have the highest risk, and predict probable enemy reactions -- all accomplished in close collaboration with the commander and his staff. Once again, these outcomes will be continuously updated as more data is received.

SOLDIER SYSTEMS Soldiers will wear, carry and ride in a formidable new ensemble of weapons, sensors, communications and protection systems. Each soldier will verbally communicate with an artificially intelligent personal assistant computer. Similar to the *Commander’s Associate*, the personal assistant will help the soldier make sense of incoming data and offer recommendations for everything from movement routes over terrain to the call for support fire. The soldier assistant can monitor all soldier biological functions, begin immediate and comprehensive first aid assistance when wounded, and notify medical personnel when assistance is required. When appropriate, the AI assistant can enhance human biological performance systems to ensure the soldier is functioning at optimum capacity in any situation presented to him.

DECIDE – *Select the best Course of Action*. As the *Commander’s Associate* becomes a trusted advisor and sounding board for the commander’s ideas and judgments, it will be an invaluable aide in laying out alternative courses of action, demonstrating the strengths and weaknesses of each, and finally presenting a recommended action with full justification. Once the decision is made, the AI associate can communicate the decision and coordinating instructions to appropriate units

Other potential soldier systems include: [14]

- Active chameleon style camouflage systems for a wide range of the EM spectrum
- Exoskeletons to augment human muscles
- Ballistic protection 5 to 10 times more effective than

current systems with correspondingly less weight

- Interactive textile/clothing that provides passive insulation and cooling; chemical and biological agent detection, protection, and decontamination; self cleaning; and electromagnetic and radio frequency shielding
- Clothing and materials that provide energy harvesting, conversion and storage
- Individual waste disposal, water recovery and recycling

LOGISTICS AND MEDICAL SUPPORT Robotics and artificial intelligence will permit the continuous monitoring of the supply and maintenance status of all equipment and units. As the logistics system automatically detects that a unit requires resupply, robotic ground and/or aerial vehicles will be dispatched to transport the requisite classes of supply directly to the using unit. With this degree of automation, some current levels of the logistics system could be eliminated. With advanced biotechnology, the soldier's health and level of performance can be continuously monitored and supported in much the same way as equipment and materiel. Medics using teleoperated surgical equipment can attend to serious wounds at the lowest echelon. The entire medical system will know almost instantly the status of all soldiers and will be prepared to accommodate wounds and injuries as quickly and proficiently as possible.

TRAINING The foremost benefit for training provided by emerging technologies will probably be virtual reality simulations that permit the rehearsal of all combat operations at a very high level of fidelity to include detailed depiction of terrain and enemy behavior. Individual and unit combat skills can be faithfully honed in highly realistic surroundings against an enemy designed to authentically respond under any environmental conditions. Virtual reality training will be similar to the aircraft simulators currently used to train airline and military pilots in all aspects of flight.

ACQUISITION The increasing speed of technological change will compel a complete revision of the current military technology acquisition processes. Technological innovations cannot be developed in isolation from doctrine, organization, training and leadership. An integrated and continuous Army transformation process must be established to optimize overall military effectiveness for a variety of missions performed in all conceivable environments.

THE DARK SIDE Technology is and always will be a double-edged sword for society. As technology becomes more advanced on the positive edge of the blade, so will it possess more potential for perils to society on the negative edge. In the wake of recent terrorist attacks, the design of new technologies requires a revision of the public safety design constraint: Public safety now has gained a higher priority in a new environment where it can no longer be assumed that individuals will take no deliberate actions that lead directly to their own demise. In some

cases, the public safety will demand a benign abort mode for all technologies with a potential for harm above a specified energy or lethality level. In other cases, access to the technology may be severely restricted and ethical standards for design engineers strictly adopted and rigidly enforced.

ETHICS AND ARMS CONTROL The importance of ethics and professional responsibility in engineering design cannot be overemphasized when weapons of mass destruction can be inexpensively and straightforwardly created by anyone with modest specialized knowledge and equipment. Arms control style agreements offer one option for halting the spread of dangerous technology applications, but these agreements will not include non-state terrorist and radical militant groups. However, arms control treaties would still be important tools to restrain the dark side of emerging technologies, and the Army could provide the prime forces for verification of compliance with international treaties and agreements. In the case of non-state sponsored militant groups, the Army could find itself a major Homeland Defense Force team member, working closely with intelligence organizations to enforce United Nations sanctioned ethical standards and controls on research into unmistakably dangerous technologies; including infectious biotechnology products, malicious information technology viruses, and other nefarious weapons.

We are only beginning to come to grips with the new mission of Homeland Defense. It is a far-reaching mission that involves extensive intelligence operations and sweeping requirements for security and special operations forces. Emerging technologies can make substantial contributions to the protection, decontamination and neutralization of biologically infectious living organisms and nanoscale mechanisms. Highly sensitive micro and nanotechnology laboratories, constructed on silicon chips using the same methods as integrated circuits, could be inexpensively produced and even woven into clothing to provide detection and decontamination.

The Army Must Meet the Challenge

The accelerating advance and increasing complexity of technology will put enormous strains on the capability of the military to adapt to an uncertain future and still accomplish its core mission of national security. The Army must embrace change and continuously transform itself not only technologically, but also in its organization, doctrine, training, and leadership. Education is the key to continuous transformation. Both individuals and organizations must become increasingly better at learning and modifying their behaviors in light of new knowledge and insights. But this is another subject beyond the scope of this article. However, the discussion must be joined now because the unrelenting advance of technology cannot be stopped.

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Polymer Nanocomposites Open a New Dimension for Plastics and Composites

Dr. Richard A. Vaia
Materials and Manufacturing Directorate
Air Force Research Laboratory

Introduction: Nanoengineered Materials

Materials and material development are fundamental to our very culture. We even ascribe major historical periods of our society to materials such as the stone age, bronze age, iron age, steel age (industrial revolution), silicon age and silica age (telecom revolution). This reflects how important materials are to us. We have and always will strive to understand and modify the world around us and the *stuff* of which it is made. The next societal frontiers will be opened not through understanding a particular material, but rather by understanding and optimizing the relative contributions afforded by material combinations.

The nanoscale, and associated excitement surrounding nanoscience and technology (NST), affords unique opportunities to create revolutionary material combinations. These new materials will enable the circumvention of classic material performance trade-offs by accessing new properties and exploiting unique synergism between materials that only occur when the length-scale of morphology and the fundamental physics asso-

ciated with a property coincide, i.e. on the nanoscale! The confluence of fundamental understanding of materials at this scale and the realization of fabrication and processing techniques that provide simultaneous structural control on the nano-, as well as micro- and macro-, length scales is the core of the exciting area of *nanoengineered materials*. Examples of such material technologies are rapidly increasing, impacting many diverse areas of the commercial and military arena.

One of the ways nanoscience has advanced the state-of-the-art has been to enhance and improve the properties of existing conventional classes of materials. Polymer composites, for example, have been a mainstay of high-performance aircraft for over a quarter century, offering a multitude of desirable (and tailorable) properties, such as high strength and stiffness, and dimensional and thermal stability. With the advent and application of nanotechnology, polymer composites could become even more attractive. As surely as polymer composites changed the face of industry twenty-five years ago, polymer *nanocomposites* will usher in a new era in materials development.

Polymer Nanocomposites Opportunities

The reinforcement of polymers using fillers, whether inorganic or organic, is common in the production of modern plastics. Polymeric nanocomposites, (PNCs) or the more inclusive term –polymer nanostructured materials, represent a radical alternative to these conventional filled polymers or polymer blends. In contrast to conventional systems where the reinforcement is on the order of microns, PNCs are exemplified by discrete constituents on the order of a few nanometers – ~10,000-times finer than a human hair. The relative size difference between conventional fillers and nanoscale fillers is illustrated in Figure 1.

Uniform dispersion of these nanoscopically-sized filler particles (or *nanoelements*) produces an ultra-large interfacial area per unit volume between the nanoelement and host polymer. For example, interfacial area approaching $700 \text{ m}^2/\text{cm}^3$ occur in dispersions of layered silicates in polymers. This is comparable to a football field within a raindrop! These dimensions also imply that the distance between nanoelements is comparable to their size. For a 1nm-thick plate, the distance between plates approaches 10 nm at only 7 vol% of plates. This is a morphology truly dominated by nanoscale features.

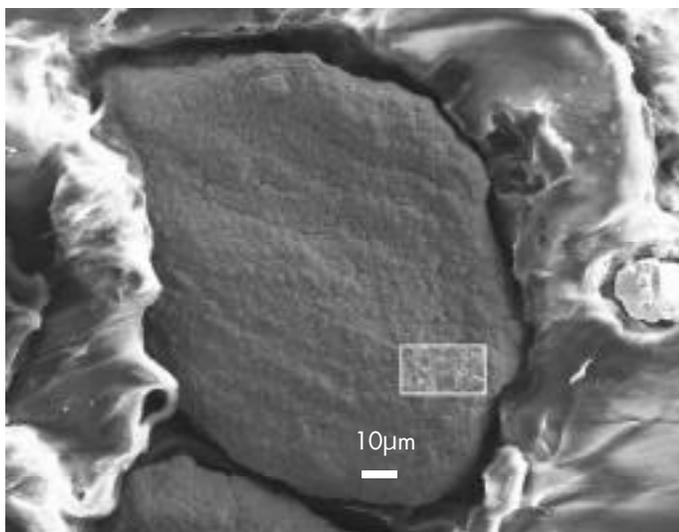


Figure 1. Scanning Electron Micrograph of Conventional Graphite Flake Filler In An Elastomer Matrix. The Inset Shows a Scanning Electron Micrograph of a Collection of ~500 Multi-wall Carbon Nanotubes (MWNT) at the Same Magnification

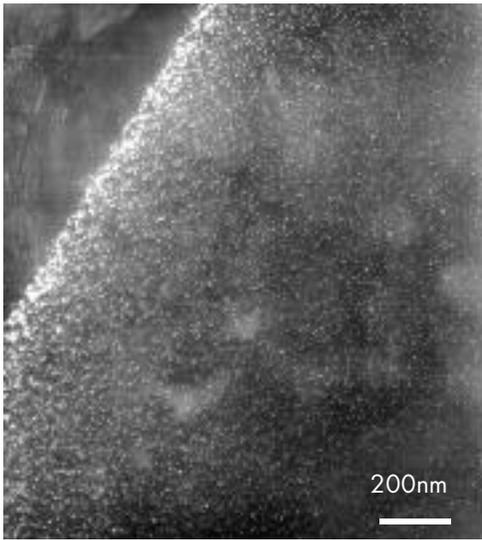


Figure 2. 7nm Ag Nanoparticles in Kapton

This immense internal interfacial area and the nanoscopic dimensions between nanoelements fundamentally differentiate PNCs from traditional composites and filled plastics. These characteristics imply the overall performance of PNCs can not be understood by simple scaling arguments that begin with the behavior of traditional polymer composites. Thus new combinations of properties derived from the nanoscale structure of PNCs provide opportunities to circumvent traditional performance trade-offs associated with conventional reinforced plastics, epitomizing the promise of nanoengineered materials.

From both a commercial and military perspective, the value of PNC technology is not based solely on mechanical enhancements of the neat resin. Rather, its value comes from providing value-added properties not present in the neat resin, without sacrificing its inherent processibility and mechanical properties. Traditionally, blend or composite attempts at ‘multifunctional’ materials require a trade-off between desired performance, mechanical properties, cost and processibility. The literature is full of examples that suggest PNC technology provides a route around these traditional limitations [1-6].

For example, consider the rapid advance of polymer-layered silicate nanocomposite (PLSN) technology. Efforts within the last 10 years have demonstrated a doubling of the tensile modulus and strength without sacrificing impact resistance for numerous thermoplastic (nylon and thermoplastic olefin {TPO}) and thermoset (urethane, siloxane and epoxy) resins through the addition of as little as 2 vol% layered silicate. Recently, General Motors and partners Basell, Southern

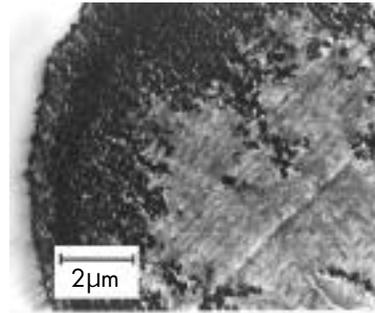


Figure 3. Ag-polybenzoxazole Fiber

Clay Products and Blackhawk Automotive Plastics announced external automotive body parts made from thermoplastic olefin-layered silicate nanocomposites. A TPO nanocomposite with as little as 2.5% layered silicate is as stiff and much lighter than parts with 10 times the amount of conventional talc filler. The weight savings can reach 20 percent depending on the part and the material that is being replaced by

the TPO nanocomposite. On a volume basis, the nanocomposite parts cost about as much as conventional TPOs because less material is needed to manufacture them and no new tooling is required to mold the parts. Overall, the weight advantage could have significant impact on environmental concerns and material recyclability. For example, it has been reported that widespread use of PLSNs by US vehicle manufacturers could save 1.5 billion liters of gasoline over the life of one year’s production of vehicles and reduce related carbon dioxide emissions by more than 10 billion pounds [6].

Considering the plurality of potential nanoelements, polymeric resins and applications, the field of PNCs is immense. Development of multi-component materials, whether microscale or nanoscale, must simultaneously balance four interdependent areas: constituent-selection, fabrication, processing, and performance. For PNCs, this is still in its infancy, and ultimately many perspectives will develop, dictated by the final application of the specific PNC. Two main fabrication methodologies have been developed for PNCs: *in-situ routes* and *exfoliation*. Currently, exfoliation of layered silicates and

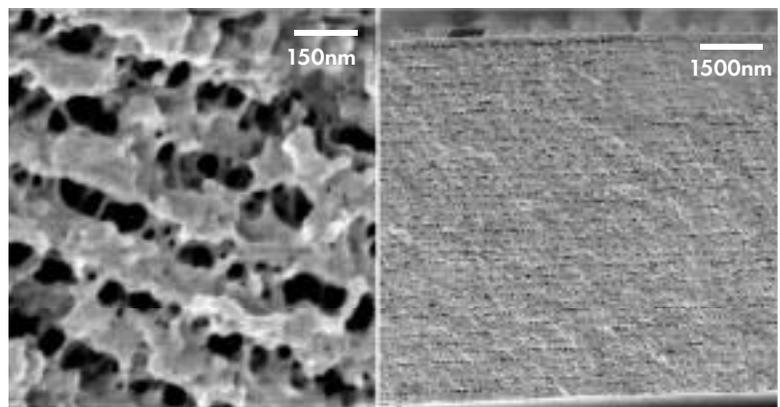


Figure 4. Liquid Crystal Nanodroplets in a Lamella Morphology

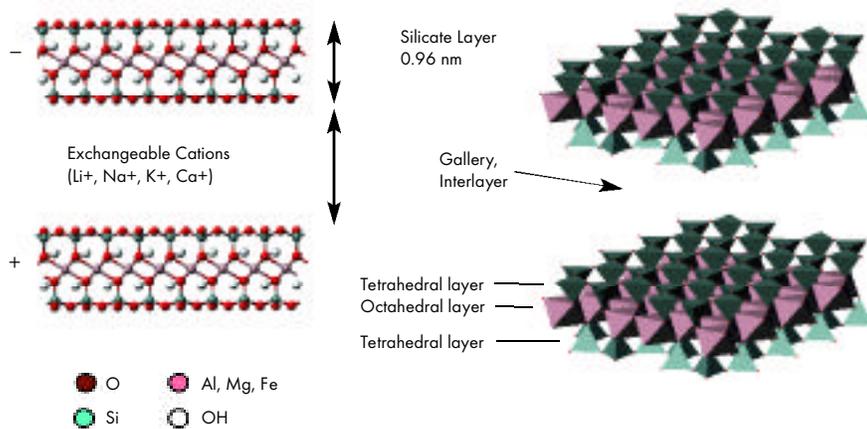


Figure 5. Crystal Structure of 2:1 Layered Silicates (Smectites) [10]

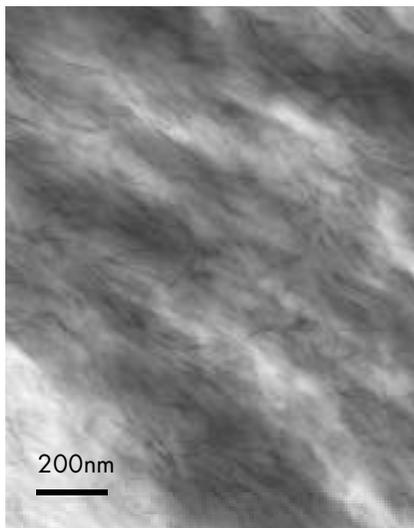


Figure 6. Nylon 6-Layered Silicate Nanocomposite



Figure 7. Comparison of Traditional Filled (bottom) vs Nanocomposite (top) Epoxy Optical Properties

carbon nanofibers / nanotubes in commodity and high performance resins are the most heavily investigated PNCs by industrial, government and academic institutions world-wide and will be further discussed below. Some examples of pre-commercial PNCs fabricated via in-situ methodologies are provided in Figures 2, 3 and 4.

In-situ PNCs

In-situ routes to PNCs are based on the creation of the nanoelement within the polymer matrix by chemical means or phase separation. The polymer matrix provides the template within which the nanoelement is formed. An example of this route is the decomposition or chemical reaction of a precursor

introduced to the polymer matrix. Figure 2 depicts 7 nm-Ag nanoparticles formed in the near-surface region of Kapton via a solution infiltration approach that is amenable to microscale pattern formation [7].

Figure 3 depicts a Ag-polybenoxazole nanostructured fiber fabricated via a comparable approach [8]. These fibers are ultra-tough, electrically conductive, ~200-times stronger and ~50% lighter than current aerospace signal wire cores. Another example of the in-situ methodology is chemical or processing perturbation of an initially homogenous polymer system comprised of a blend of two or more chemically discrete constituents to induce a controllable nanoscale phase separation of the constituents.

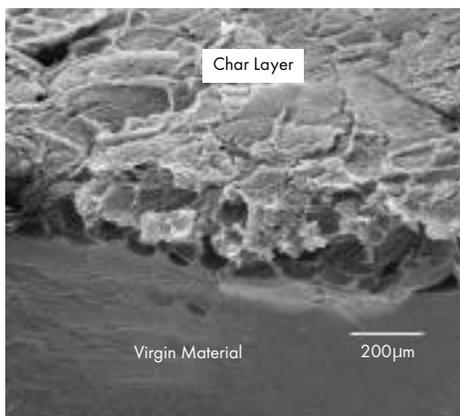


Figure 8a

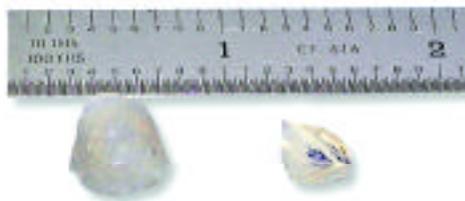


Figure 8b

Figure 8. Demonstration of PLSN Self-passivation Behavior

Figure 4 depicts ~70 nm liquid crystal droplets organized within a lamella morphology with ~200nm layer spacing formed via holographically-induced liquid crystal phase separation from a photopolymerizable syrup at two magnifications. These structures result in ultrafast (ms) switchable diffractive optics and filters that have military applications. Similar behavior has been demonstrated for patterning nanoparticles in photopolymerizable syrups [9]. The interested reader is encouraged to examine the associated references [7-9] and explore related efforts in the literature to disperse, arrange and/or in-situ form quantum dots, oxide nanoparticles, metallic nanoparticles, nanowires, proteins, enzymes, etc. in polymer hosts.

Layered Silicates

Layered silicates (alternatively referred to as 2:1 layered aluminosilicates, phyllosilicates, clay minerals and smectites) are the most commonly used inorganic nanoelements in PNC research to-date. Layered silicates possess the same structural characteristics as the well-known minerals talc and mica and are com-

prised of hydrated aluminosilicate [10]. Their crystal structure and habit are summarized in Figure 5.

In the figure, the Van der Waals interlayer (or gallery) containing charge-compensating cations (M^+) separates covalently bonded oxide layers, 0.96 nm thick, formed by fusing two silica tetrahedral sheets with an edge-shared octahedral sheet of either alumina or magnesia. The charge per unit cell (generally between 0.5 and 1.3) originates from isomorphous substitution within the silicate layer (e.g. tetrahedral Si^{4+} by Al^{3+} or octahedral Al^{3+} by Mg^{2+}). The number of exchangeable interlayer cations is also referred to as the *cation exchange capacity* (CEC). This is generally expressed as milliequivalents/100g, and ranges between 60 and 120 for relevant smectites. Variation in the amount, type and crystallographic origin of the excess layer charge results in a large family of natural (e.g. montmorillonite, hectorite, saponite) and synthetic (e.g. Laponite, fluorohectorite) layered silicates exhibiting different physical and chemical characteristics, such as layer size, stacking perfection, reactivity and Lewis acidity. For example the lateral dimension of the layers range from 20 to 1000 nm.

When exfoliated, an individual sheet is 1 nm thick, with aspect ratios (diameter:thickness) in excess of 100. Conceptually, the process of layered silicate dispersion in polymers can be likened to removing, and then arranging, millions of sheets of paper from thousands of tomes on library shelves to uniformly occupy all the free space in the library. The highly anisotropic structure of the silicate layer is critical to provide percolative behavior at low volume fractions, which manifests in numerous physical property increases at small amounts of dispersed layers. Figure 6 depicts the morphology of a Nylon 6-layered silicate nanocomposite [11]. Dark lines are individual layers of aluminosilicate, 1 nm thick, oriented perpendicular to the sample surface. This structure results in enhanced mechanical properties at elevated temperatures, opening new opportunities for plastics in the automotive industry [6], as well as reduced water and CO_2 permeability, enabling improved food and beverage packaging [4].

In general, nanoscale dispersion of the layered silicate platelets in resins produces glassy modulus enhancements of one to two times and rubbery modulus increases of 5-20 fold. Related increases in heat distortion temperature and enhanced elevated temperature mechanical properties (strength and modulus) are commonly reported. Additionally, reduced thermal expansivity (CTE), matrix swellability, gaseous permeability and flammability upon 1-5 vol% addition of exfoliated layered silicates will provide new opportunities for various resin systems. An abridged list of polymers investigated with layered silicate includes polystyrene, various polyamides (6, 6-6, 11, 12, MDX), polyimides, polypropylene, ethylene vinyl acetate copolymers, poly(styrene-b-butadiene) copolymers (SBS), elastomers (PDMS, EPDM, NBR), polyurethanes, poly(ethylene oxide), poly(vinyl alcohol), polyaniline, epoxies, and phenolics. Alexandre et al. [5], Beal and Pinnavaia [2], and Krishnamoorti and Vaia [3] provide summaries of some of the polymers and fabrication routes available in the open literature. The bottom line is that these unique property combinations are observed

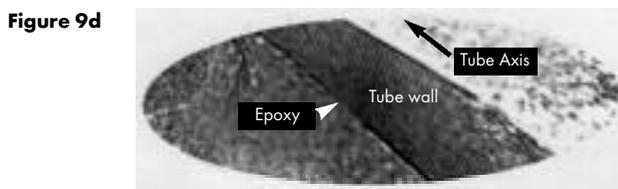
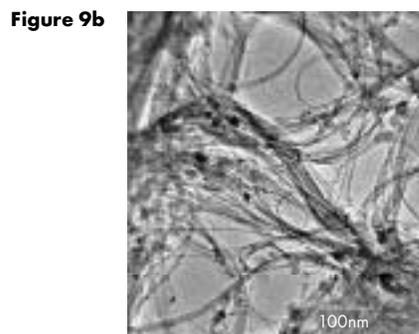


Figure 9. Images of Single- and Multi-walled Carbon Nanotubes

with surprisingly low volume fraction additions of layered silicate (1-5%), thus maintaining polymeric processibility and reducing weight with respect to micron-scale counterparts (>20% loading). Note that these comparisons are with regard to conventional filled polymers and not with regard to continuous fiber reinforced composites. PNCs may provide enhanced, multi-functional matrix resins, but should not be construed as a potential replacement for current state-of-the-art carbon-fiber reinforced composites.

From the military perspective, these enhanced polymer systems provide opportunities in many venues. In addition to a general desire for higher-performance, higher use-temperature resins and thermoplastics, PLSNs provide opportunities to address material limitations in advanced system concepts. Combinations of reduced impact resistance, CTE control, suppression of microcracking and increased modulus are currently being examined for next-generation nanoscale rigid-particulate reinforced resins for advanced fiber reinforced polymeric composites in unmanned aerial vehicles [12]. Thermal stability and enhanced fire retardancy through char formation have motivated investigation of PLSNs as a component to anti-flammability additives for aircraft interiors [13]. Superior barrier properties against gas and vapor transmission have resulted in applications for food and beverage packaging for military rations [14] and for barrier liners in storage tanks and fuel lines for cryogenic fuels in aerospace systems. Also, depending on the type of polymeric host, PLSNs display interesting ionic conductivity for solid-state electrolytes in batteries [15]. Finally, along with enhanced scratch resistance and ballistic performance, the nanoscopic phase dimensions and low volume fractions enable maintenance of optical clarity, critical for scratch-

resistant face shields. Figure 7 compares the optical properties of traditional filled and nanocomposite epoxy. In the figure the optical clarity of exfoliated nanoscale morphology (top) is substantially better than the intercalated, conventional filler morphology at comparable loadings (bottom). Recent efforts have begun to explore use of layered silicates as ceramic precursors that will react in-situ with aggressive environments to form a tough ceramic passivation layer on the polymer surface. Examples of such self-passivation/self healing during exposure to a solid-rocket motor exhaust (top) and plasma environments (bottom) [16] are shown in Figure 8. Combinations of the self-passivation response with CTE control provide unique alternatives to current materials being examined for inflatable membranes for space antennas and solar collectors. Survivability in real space environments is currently being examined for PLSNs and other polymer nanocomposites through an exposure experiment on-board the International Space Station [17].

Carbon Nanotubes

In contrast to the 25+ year investigation of layered silicate dispersion in polymers, exploration of carbon nanotubes dispersion is relatively new, hindered until recently by the limited availability of nanotubes. However, nanotube-polymer nanocomposites are garnishing substantial attention today because carbon nanotubes offer opportunities to impart unique electrical and thermal properties to the polymer resin as well as to enhance mechanical and physical response. Figure 9 briefly summarizes the structural aspects of carbon nanotubes [18]. Tube diameters can range from 1-100 nm with aspect ratios (length : diameter) in excess of 100 or 1000! As with the layered silicates, the highly anisotropic nature of the tube is criti-

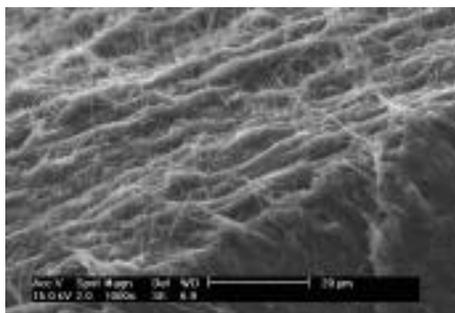


Figure 10. Scanning Electron Micrograph of MWNT Dispersion In Silicone Matrix [20]

cal to provide percolative behavior at low volume fractions, resulting in graphite-like electrical and thermal properties at 1-2 vol% additions.

Overall, carbon nanotubes (i.e. nanoscopically hollow fibers) are generally considered in two categories: single wall nanotubes (SWNT) and multi-wall nanotubes (MWNT). SWNTs are comprised of an individual graphene sheet (Figure 9a). The individual tubes nominally aggregate into ‘ropes’ consisting of face-center packed individual tubes. Figure 9b shows a transmission electron micrograph (TEM) of a random mat of these SWNT ropes (Figures 9a and 9b courtesy of R. Smalley, cnt.rice.edu/pics.html.) Substantial technological excitement surrounds single-wall carbon nanotubes, based on theoretical prediction and initial experimental verification of incredible mechanical properties ($E \sim 1$ TPa [19]) and metal-like electrical conductivity [18] of individual tubes. MWNTs are comprised of nested single-wall tubes (Figure 9c). The external surface of a MWNT is a graphene plane and the individual graphene sheets within the tube interact via van der Waals forces. Alternative gaseous MWNT fabrication routes also produce a bamboo-like structure (Figure 9d) comprised of short segments containing nested tubes with a finite orientation with respect to the overall MWNT axis (courtesy Applied Sciences, Inc.). Terminal strained graphene sheets decorate the surface of these tubes, providing chemical sites for facile surface functionalization and interfacial tailorability.

Challenges associated with the development of low-cost manufacturing approaches, the processibility of raw SWNT products and the maintenance of the SWNT properties during nanotube-polymer fabrication and processing is limiting rapid success of SWNT as polymer nanofillers. Current prices range from \$500-\$1000 per gram for purified SWNTs. Nonetheless, substantial academic and government investigations are currently addressing these issues.

In contrast, the commercial availability of multiwall nanotubes (MWNT) at \$60-\$100 per pound is facilitating exciting successes today. Motivated by similar product considerations as discussed for the PLSN systems (provide comparable mechanical properties as achieved with microscale fillers, but at lower

loadings, while maintaining processibility and delivering additional functionality), numerous pre-commercial successes have been reported. For example, MWNTs have been used as direct replacements to carbon-black in paint powders, providing sufficient electrical conductivity at an order of magnitude lower filler loading to enable electrostatic powder coating of automotive parts (e.g. Hyperion Catalysis Int.). The ability to chemically tailor the external surface of the tube while maintaining complete graphene planes within the tube core provides substantial flexibility to independently tailor mechanical, electrical and interfacial properties. A potential drawback to MWNTs relative to SWNTs is decreased mechanical reinforcement because of the weak bonding between the graphene planes within the tube. However, current applications driving nanotube reinforced plastics appear to be motivated more by addition of electrical and thermal properties than by substantial (10-100x) mechanical property increases, and thus MWNTs are expected to make substantial contributions in this arena. Figure 10 shows homogeneously dispersed carbon MWNTs in an elastomer matrix, providing a conductive plastic with elastomeric extensibility in excess of 500% [20].

From the military perspective, tailoring electrical or thermal conductivity of polymer films, fibers or monoliths with very low loadings provides revolutionary opportunities, spanning from electro-magnetic shielding to thermally conductive composites to electrostatic discharge layers to smart fabrics for the future soldier. Furthermore, since these nanocomposites can be tailored to be responsive to applied electrical fields, a range of adaptive structures is envisioned. Even more revolutionary is the concept of using the nanoscale percolative network of tubes to controllably remove or transport electrical charge to nanoscopically structured polymer regions between the tubes, providing the foundation for technologies ranging from next-generation flexible photovoltaics to conformal antennas to energy storage devices. The potential impact is pervasive, even greater than that envisioned for PLSNs.

Challenges

Notwithstanding the considerable advances, excitement and promise of exfoliated PNCs, substantial fundamental research is still necessary to provide a basic understanding of these materials to enable full exploitation of their nanoengineering potential. Despite the large number of combinations of matrices and potential reinforcing nanoelements with different chemistry, size, shape and properties, all PNCs share common features with regard to fabrication methodologies, processing, morphology characterization and fundamental physics.

The objective of PNC fabrication via exfoliation methodology is to uniformly disperse and distribute the inorganic filler, initially comprised of aggregates of the nanoparticles, within the polymer. The final PNC structure results from the transformation of the initially microscopic heterogeneous system to a nanoscopically homogenous system. In general, four approaches have been developed to fabricate PNCs via exfoliation - *solution processing*, *mesophase mediated processing*, *in-situ polymeriza-*

tion and melt processing. Each methodology has advantages with respect to the processing steps necessitated by the desired final form of the PNC (powder, film, paste, fiber, bulk monolith). Substantial research efforts currently endeavor to address the fundamental challenge of providing general guidelines, including thermodynamic, kinetic and rheological considerations for morphology control via these fabrication processes. For example, many potential military opportunities depend on successful incorporation of the nanoelements in thermoset resins. Surface functionalization must be carefully chosen to control polymerization rates and initiation points such that separation of the aggregate of nanoelements occurs before or during polymerization. This is because the extent of cross-linking reactions determines the gel-point of the matrix, and ultimately the extent of exfoliation, hence the final PNC morphology [21]. Additional complications arise from preferential partitioning of the various chemical components in these multicomponent resin systems (reactive oligomer, prepolymer, cross-linker, catalyst, etc.) to the nanoelement surface modifying reactivities and creating unknown gradients in network topology.

The key to any of these fabrication processes is the engineering of the polymer-nanoparticle interface. Surfactants are commonly used to facilitate this process. These range from small molecules ionically associated with the nanoparticle surface, such as with layered silicates, to chemically bound small molecules or physi-absorbed polymers for nanotubes. These surface modifiers mediate interlayer interactions by effectively lowering the interfacial free energy. Furthermore, they may serve to catalyze interfacial interactions, initiate polymerizations, or serve as anchoring points for the matrix and thereby improve the strength of the interface between the polymer and inorganic filler. However, choice of the optimal modifier to date is at best empirical. Most efforts currently focus on developing interfacial tailoring that achieves dispersion. This is done without regard to providing the necessary thermal stability and desired interfacial response for final form processing, or without a priori determination of the desired interfacial characteristics (e.g. strong, intermediate or weak bonding) to maximize material performance. However, these later considerations are paramount to providing components that have a reliable service life.

Developing an understanding of the characteristics of this interphase region, its dependence on nanoelement surface chemistry, the relative arrangement of constituents, and ultimately its relationship to the PNC properties is a current research frontier in nanocomposites. Equally important is the development of a general understanding of the morphology-property relationships for mechanical, barrier and thermal response of these systems. This necessitates determining the critical length and temporal scale at which the continuum description of a physical process gives way to mesoscopic and atomistic views of these nanoscale systems. This is one of the current challenges for the burgeoning field of computational materials science (see AMPTIAC newsletters Vol. 5, #2 and Vol. 5, #3 for extensive information on the topic of Computational Materials Science).

Summary

Polymer nanocomposites is a rapidly growing area of nano-engineered materials, providing lighter weight alternatives to conventional, filled plastics with additional functionality associated with nanoscale specific, value-added properties. If the promise and excitement surrounding layered silicates and carbon nanotubes are any indication, the future of PNC technology is truly boundless. The opportunities to extend PNC concepts to other nanoelements and polymer hosts are immense, opening the way to provide tailor-made materials that circumvent current limitations and enable future concepts for the DOD and the defense community at large.

Acknowledgements

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Dr. Vaia received a Ph.D. from Cornell University (Dr. Emmanuel Giannelis, Materials Science and Engineering) in 1995, following a M.S. and B.S. in Materials Science from the Materials and Engineering Department at Cornell. He currently holds 3 patents, is the editor of one book, and has published over 40 peer-reviewed journal articles in nanomaterials and nanotechnology.

Power from the Structure Within: Application of Nanoarchitectures to Batteries and Fuel Cells

Dr. Richard T. Carlin
Director of the Mechanics and Energy Conversion Division
Office of Naval Research

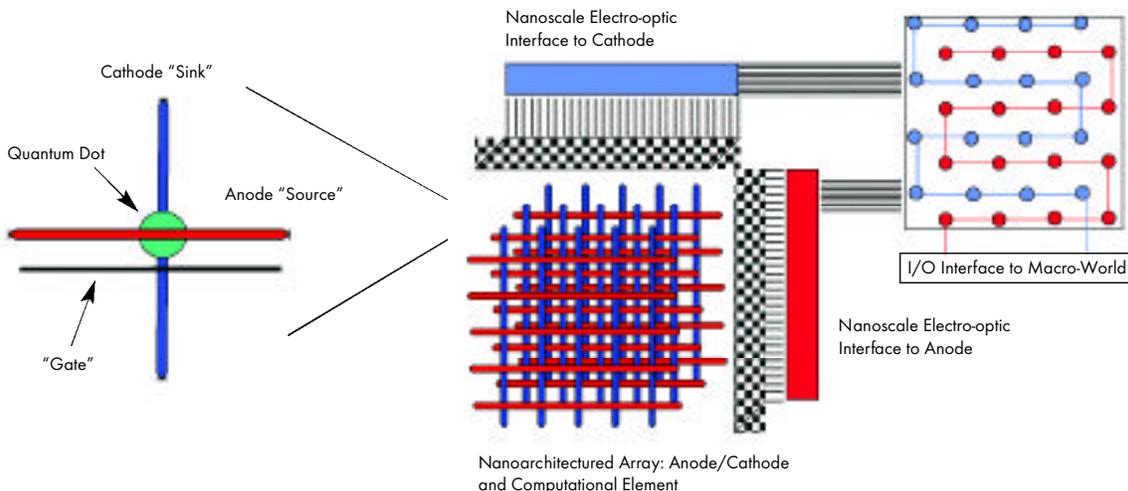
Dr. Karen Swider-Lyons
Chemistry Division
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Introduction

The use of nanomaterials for energy storage and conversion in electrochemical power sources is a rapidly growing field with tremendous potential. Even though the use of nanomaterials in power sources is not new, the science at the nanoscale has still not been fully exploited. A prime example is the use of highly dispersed nanoscale platinum particles (and more recently alloys or mixed-metal systems) as effective electrocatalysts in fuel cells. Although fuel cells have used nanoscale platinum catalysts for decades, their performance improves yearly as scientists learn to control and modify the nanoscale catalysts in the electrode structures [1]. Due to advances in analytical instrumentation and modeling, the complex electrocatalytic processes in fuel cells, which require concurrent electronic and ionic transport with simultaneous catalytic activation at the nanoscale, are beginning to be addressed in a scientific manner, as opposed to previous empirical approaches.

The challenges and opportunities for nanoscience in power sources lie in the understanding, control, and fabrication of complex structures and composites at the nanoscale. Only after engineers and scientists have gained a strong footing in these areas will it be possible to fully realize and exploit the capabilities of this technology. Certain phenomena are only possible on the nanoscale due to the dominance of interfacial physics and chemistry at large surface-to-volume ratios, such as the quantum interactions between nanoscale material phases. By learning to control the physics and chemistry at these small length scales, one can envision *nanoarchitected* materials engineered to exhibit properties and performance that far exceed the “sum of the parts.” One such revolutionary approach would be the implementation of an array of individual electroactive nanoarchitectures performing ultra-fast computations, using single-electron “bits” shuttled between a nanoscale electron storage source and driven by nanoscale electrochemical voltage sources.

Figure 1. A Conceptual Nanoarchitected, Integrated Battery-computer with Electro-optic Interfaces to the Macro-world



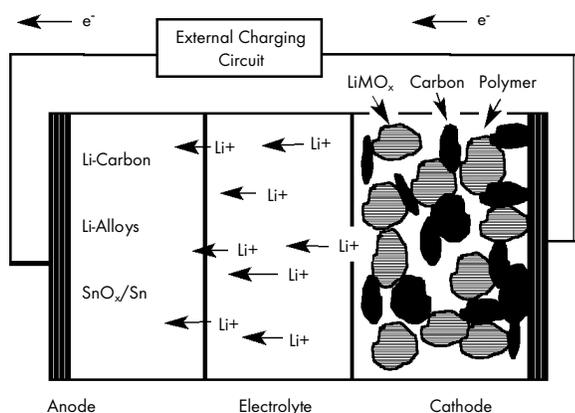


Figure 2. Illustration of a Lithium-ion Cell
(Figure Courtesy of D. Sadoway and A. Mayes, Massachusetts Institute of Technology)

Nanoarchitected electro-optic devices could be used for internal interconnects and to connect the array to the microscale world for data input-output and intermittent recharging. Such a complex nanoarchitecture would remove the limitations of electron transport between functioning nanoscale components. The concept is illustrated in Figure 1.

The potential revolutionary benefits of nanoarchitected power-source materials, composites, and eventually multifunctional structures, make them prime strategic research areas. To exploit these potential benefits, the Office of Naval Research (ONR) and the Naval Research Laboratory (NRL) have embarked on the challenging path to develop these concepts. This article provides examples of research directed toward understanding, controlling, and fabricating complex structures and composites for battery and fuel cell applications. Such research is only in its infancy and is likely to undergo dramatic evolutionary and revolutionary changes as insight into nanoarchitectures becomes clearer through scientific investigations in all research areas. While the examples presented here come primarily from work supported by ONR, a tremendous amount of similar and related research is ongoing around the world and is introduced where appropriate. Recent insightful overviews on electrochemical applications of nanomaterials have

appeared, including topics on aerogels [2], nanostructured battery materials [3], production of nanostructured electroceramics [4], and nanostructured solid-state electrolytes [5].

Batteries

Battery cells are fundamentally composed of three active components: an anode (negative electrode), a cathode (positive electrode), and an electrolyte. The functions of the anode and cathode are to store, release, and reincorporate electrons and charge-balancing ions during discharge and charge cycles, thus the electrodes must possess both high ionic and electronic conductivities. The amount of electrical charge stored by an electrode is referred to as the *electrical capacity*, typically expressed either in units of amp-hours per kilogram (Ah/kg) or amp-hours per liter (Ah/l). Electrical capacity is multiplied by the electrochemical potential of the battery to obtain its total available energy on a weight or volume basis, typically expressed in units of Watt-hours per kilogram (Wh/kg) or Watt-hours per liter (Wh/l) respectively. The electrodes interchange ions in a cell through an electronically insulating electrolyte (liquid or solid) that has high ionic conductivity to minimize internal battery resistance. Cells are used individually or linked in series or parallel to meet the capacity and energy requirements of an external load. Additional information on batteries is readily available from many resources [6-9].

The focus of many current battery research and development programs is lithium-ion and lithium-metal batteries [9]. The cathodes for both these cell chemistries typically contain a transition-metal oxide lithium-insertion compound, such as LiCoO_2 . The anodes for lithium-ion batteries are usually a lithium-carbon insertion compound or a lithium-metal alloy, while metallic lithium is employed as the anode in lithium-metal batteries. Either an organic liquid or a solid-state lithium-ion conductor serves as the electrolyte in both lithium-ion and lithium-metal batteries. During operation, lithium ions shuttle between the electrodes through the electrolyte, while electrons are driven through the external electrical circuit by the electrochemical potential (typically 3 to 4 V). A Lithium-ion battery being charged is depicted in Figure 2.

Lithium Battery Anodes

Lithium metal offers the highest theoretical specific capacity of any anode material (3,862 Ah/kg), but dendrite formation dur-

Figure 3. High-resolution TEM of 1:2 Mole Ratio Si/TiN Nanocomposite Anode

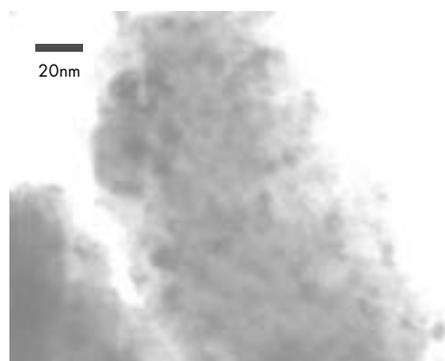
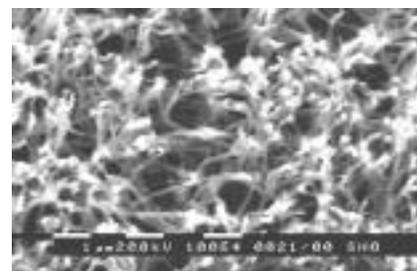


Figure 4. High Li-capacity Templated Anode Consisting of 110-nm Diameter SnO_2 Nanofibers [15]



ing cycling has thus far prevented its practical use in rechargeable batteries. Dendrite formation can lead to cell shorting and to the formation of small particles of metallic lithium that can undergo detrimental, exothermic reaction with the organic electrolytes. Lithium alloys are viable options for high-capacity anodes (LiAl alloy: 993 Ah/kg and 2,681 Ah/l based on the weight and volume of Al, respectively); however, most of the desirable alloying metals undergo large dimensional changes upon lithium alloying that cause fragmentation and rapid capacity loss during cycling. Most current battery development therefore focuses on lithium-ion chemistries with graphitic anodes having theoretical weight and volume electrical capacities of 372 Ah/kg and 837 Ah/l, respectively.

Recently, researchers have discovered that nanoscale tin (Sn) particles encapsulated in an inert inorganic matrix can undergo reversible lithium alloying over many cycles with minimal losses in capacity [10]. Some examples of these nanocomposite anodes include Sn-B_{0.56}P_{0.4}Al_{0.42}O_{3.6} glass (600 Ah/kg, 2,200 Ah/l) [10], Sn₂Fe-SnFe₃C (620 Ah/kg, 1,600 Ah/l) [11], and Sn-Li₂O (600 Ah/kg) [12]. The exact role that the nanocomposite structure plays in anode cycle-life and capacity is not well understood and is an active area of research [3].

With the identification of appropriate nanoscale structures, new nanocomposite materials are being designed for use as high-performance lithium-ion anodes. For instance, Professor Prashant Kumta's research group at Carnegie Mellon University is fabricating nanoscale composites of silicon (Si) and titanium-nitride (TiN) with high lithium capacities [13]. The Si phase reversibly alloys with lithium to form a high capacity storage medium, while the TiN phase is non-reactive with lithium, but has high mechanical strength to prevent cracking, and is a good electrical conductor ($2-5 \times 10^4 \text{ }^{-1} \text{ cm}^{-1}$). When mixed together at the nanoscale, the Si/TiN composite has the electrical and mechanical properties needed for a high-capacity lithium anode. A 1:2 mole ratio Si:TiN nanocomposite obtained after 12 hours of high energy mechanical milling (HEMM) exhibits a stable capacity of 300 Ah/kg. This is lower than the theoretical value of 776 Ah/kg, calculated assuming complete reaction of Si with 4.4 molar equivalents of Li; however, the experimental volumetric capacity of 1,100 Ah/l exceeds that of a lithium graphite electrode by 30%. A high-resolution transmission electron micrograph (TEM) of a 1:2 mole ratio Si/TiN

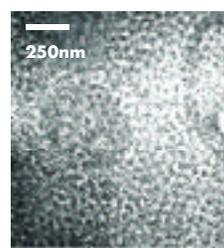


Figure 5a

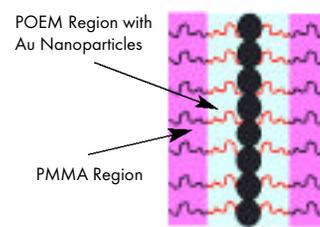


Figure 5b

Figure 5. (a) TEM of POEM-b-PMMA Containing a Precursor Gold Salt (LiAuCl₄)

(b) A Conceptualization of a Highly Reversible Self-organizing Nanocomposite Electrode (SONE)

nanocomposite is shown in Figure 3, in which the dark spots are electrically conducting TiN nanoparticles of <20 nm diameter embedded in an amorphous Li-ion conducting Si phase. From TEM and x-ray diffraction studies, it appears that the nanocomposite consists of nanoscale TiN particles embedded in an amorphous Si phase. Ongoing work intends to increase the lithium capacity and overall performance of the Si/TiN anode using various strategies, including determining and eliminating the sources of interfacial resistances between the Si and TiN nanoparticles.

Another promising developmental approach to nanoarchitected lithium-alloy anodes is to use templated nanostructures to fabricate nanoscale materials having the specific sizes and dimensions needed for optimum performance. This work was pioneered by Professor Charles Martin (University of Florida, Gainesville) with support from ONR [14]. One example is a templated anode consisting of 110-nm-diameter SnO₂ nanofibers (shown in Figure 4) irreversibly reduced to a Sn-based nanocomposite. This anode is capable of 800 reversible charge-discharge cycles with capacities exceeding 700 Ah/kg [15]. In addition, discharge rates are an order of magnitude greater than those achieved in conventional lithium-ion anodes, and capacity losses of the nanocomposite anode are minimal at these rapid discharge rates. The performance of these nanoarchitected anodes is attributed to the small size of the individual nanofibers and to the small domain size of the Sn grains within the nanofibers.

Lithium Battery Cathodes

Numerous materials have been studied for use as lithium-metal and lithium-ion battery cathodes, including metal oxides, metal sulfides, conducting polymers, and polysulfides. Transition-metal oxides are the most successful materials because of their chemical and structural stability, high lithium-ion capacity, and favorable electrical properties (such as high conductivity of lithium-ions and electrons). Table 1 summa-

Table 1. Performance of Selected Transition-metal Oxides as Lithium-ion Battery Cathodes

Cathode Material	Theoretical Capacity (Ah/kg)	Practical Capacity (Ah/kg)	Average Cell Voltage (V)
LiCoO ₂	274	142	3.6
LiNiO ₂	275	145	3.6
LiNi _{0.8} Co _{0.2} O ₂	274	180	3.6
LiMn ₂ O ₄	148	120	3.8

izes the theoretical and practical performance of state-of-the-art metal oxide cathode materials. The theoretical capacity is calculated from the total lithium-ion content of the compound, whereas the practical capacity corresponds to the actual amount of lithium that can be reversibly intercalated. (Cell voltages quoted in Table 1 assume a lithium-graphite anode.) The practical lithium capacity of the oxides is lower than the theoretical lithium capacity, because the metal-oxide structures allow only a portion of the lithium ions to be reversibly accessed during electrochemical cycling.

In addition to the materials listed in Table 1, the lithium-ion intercalation properties of vanadium oxides have attracted a great deal of interest. The vanadium oxides display a range of V:O molar ratios (*e.g.*, V_2O_5 , V_3O_8 , and V_6O_{13}) and possess good lithium capacity; however the voltage of the VO_x is lower (-2-3 V) than the other metal oxides (-3-4V). Recently, nanophase V_2O_5 cathode materials have been prepared with capacities up to 450 Ah/kg and a corresponding specific energy of approximately 1,500 Wh/kg when coupled with a lithium metal anode [2, 9]. Other nanophase cathode materials, including some in Table 1, show increased capacities compared to the same compositions having micron-scale particles. This has been attributed to facile Li^+ diffusion into the interior of the nanoparticles with a concomitant reduction in electrode polarization.

The nanoscale vanadium oxides discussed above have suffered from capacity loss during cycling, however, ongoing research support by ONR is helping to resolve this problem. Recently, Professor Bruce Dunn's research group at UCLA produced V_2O_5 nanocomposites, in which carbon nanotubes are used to electrically "wire" the poorly conducting vanadium-oxide nanoparticles. The benefits are dramatic when this nanoarchitected approach is used: the practical capacity of the wired vanadium-oxide exceeds 400 Ah/kg, which is 2 to 3 times that of current cathode materials, and there are no capacity losses observed over 20 cycles at high discharge rates.

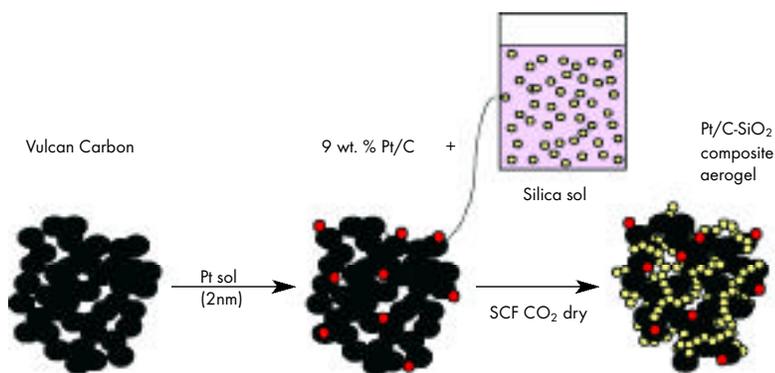


Figure 6. Nanoarchitected Pt/C-SiO₂ Electrocatlysts Prepared using Sol-Gel Techniques (SCF is supercritical fluid)

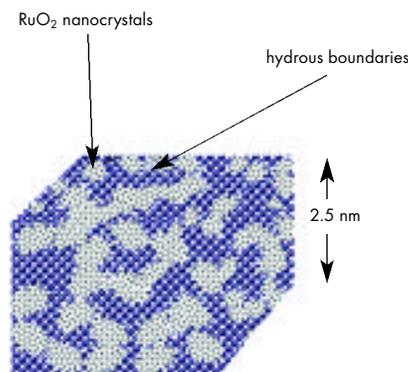


Figure 7. "Natural" Nanocomposite of Intertwined RuO₂ Nanocrystals and Hydrrous Proton-Conduction Regions

More recently, Professor Dunn has demonstrated a high reversible capacity for magnesium ions in the V_2O_5 cathodes ($1.5 Mg^{2+}$ per V_2O_5). The electrochemical intercalation of the large Mg^{2+} ions is not possible with mesoscale vanadium oxides. This is a key discovery because the double-charge of Mg^{2+} carries almost twice the energy of Li^+ , hence the development of this concept may lead to magnesium-based rechargeable batteries that offer high capacities and are inherently safer than lithium batteries.

Electrolytes

Two successful approaches in the development of nanoarchitected polymer electrolytes for high-capacity lithium-ion batteries are to incorporate inorganic nanoparticles into a conventional polymer electrolyte (*e.g.* polyethylene oxide with lithium salt) or to create block copolymers that self-organize into nanophase regimes that synergistically provide lithium-ion conductivity and structural stability. With regard to the former approach, nanoparticle guests, such as $LiAlO_2$, Al_2O_3 , TiO_2 , and SiO_2 , improve the performance of polymer electrolytes. The nanoparticles disrupt the polymer-chain organization and create lithium ion conducting pathways by promoting Lewis acid-base interactions between the inorganic nanoparticle and the polymer segments [16]. These effects result in lithium-ion electrolytes with increased lithium-ion conductivity and an enhanced lithium-ion transport number, and in addition, the nanoparticles stabilize the lithium-polymer interface [16].

Professors Anne Mayes and Donald Sadoway at MIT have been

exploiting the elegant nanoarchitectures of block copolymers to improve the performance of lithium-polymer batteries [17]. They employ poly[oligo(oxy-ethylene) methacrylate]-*b*-poly-(methyl methacrylate), or POEM-*b*-PMMA, with LiCF₃SO₃ salt as a polymer electrolyte in a Li/polymer/amorphous VO_x cell to achieve cathode capacities of 400 Ah/kg over 200 cycles and projected cell energy densities of >350 Wh/kg. These block copolymers are effective lithium-ion electrolytes because the hydrophilic oxy-ethylene regions transport lithium ions, while the hydrophobic regimes provide structural stability plus a “trap” to inhibit transport of hydrophobic anions (i.e. hydrophobic anions will stay in the hydrophobic regions away from the hydrophilic regions), and thus increase the lithium ion transport number.

The Mayes and Sadoway research groups have also prepared self-organizing nanocomposite electrodes (SONEs) in which gold nanoparticles are incorporated into the lithium-ion conducting regions to serve as highly reversible lithium-gold alloy anodes. The segregation at the nanoscale of the gold-precursor salt into the POEM region of the block copolymer structure is shown schematically in Figure 5a. The salt becomes segregated within the relatively hydrophilic POEM regions and becomes visible as the dark regions in the TEM micrograph. Upon electrochemical reduction, the gold-precursor salt is reduced to metallic gold nanoparticles, as illustrated in Figure 5b. The gold nanoparticles then can undergo highly reversible charge-discharge cycling (>700 cycles). The preparation of SONEs that incorporate other lithium-alloying nanoparticles, such as aluminum, tin, and silicon, may lead to the development of low-cost, practical, high-performance nanoarchitected anodes for lithium-ion polymer batteries.

Fuel Cells

As with batteries, fuel cells are composed of an anode, a cathode, and an electrolyte. However, the anode and cathode do not store charge but rather electrocatalytically activate a fuel (e.g., hydrogen) at the anode and an oxidizer (e.g., oxygen) at the cathode. Effective electrocatalysis at the electrodes requires concurrent ionic and electronic transport [1]. Achieving these simultaneous dynamic processes requires the intersection of multiple phases, including the electrocatalyst (e.g., Pt), an ion conductor (liquid or solid-state), an electronic conductor (e.g., carbon powder), and the gas. By controlling the intersection of these regions at the nanoscale, dramatic improvements in fuel-cell performance can be achieved. In addition, the fuel cell electrolyte can be enhanced through nanoscale structural optimization. In fact, the archetypal proton exchange membrane (PEM) fuel cell electrolyte, Nafion™, is itself a nanostructured material, possessing nanoscale hydrophilic regions that conduct protons and fluorinated hydrophobic regions that provide structural stability [1].

ELECTROCATALYSIS Ongoing research at NRL has provided valuable insight into how the design of nanostructured electrocatalytic architectures can improve fuel cell performance. Dr. Debra Rolison and co-workers at NRL have prepared nano-

architected Pt electrocatalysts in a systematic manner using sol-gel techniques (illustrated in Figure 6; for additional information, see reference 18). The Vulcan carbon powder provides a continuous electronic network to the 2-nm carbon-supported colloidal Pt nanoparticles within an architecture defined by the continuous nanoscale network of the SiO₂ aerogel. The continuous 3-D mesoporous path provides a flux of fuel to the Pt electrocatalyst, resulting in a >10,000x increase in its catalytic activity for methanol oxidation. This approach emphasizes the advantages of designing a multifunctional nanoarchitected site to improve the performance of fuel-cell catalysts.

Advancements in analytical methods are also leading to improvements in the development of active nanostructures. NRL's Dr. Karen Swider-Lyons and co-workers in collaboration with Professor Takeshi Egami and Dr. Wojtek Dmowski at the University of Pennsylvania have used advanced structural analysis methods to demonstrate that the electrochemical properties of hydrous ruthenium oxide are due to its innate nanocomposite nature. Diffraction methods show that this “natural” nanocomposite is composed of nanoscale wires of electronically conducting RuO₂ nanocrystals that are surrounded by hydrous proton-conducting regions [19], as shown in Figure 7. The intimate mix of electronic and protonic conduction in this nanocomposite material explains its high activity as a co-catalyst for carbon monoxide-tolerant Pt-RuO_x fuel cell electrocatalysts [1] and is key to understanding the performance of hydrous ruthenium oxide as a pseudocapacitor [2]. Understanding the relationship between the nanoscale structure and electrochemical properties in materials will also lead to the design of other active materials for electrochemical power sources.

ELECTROLYTE As mentioned earlier, PEM fuel cells already employ the nanocomposite electrolyte Nafion™. Perhaps even more interesting, however, is the potential for nanoarchitected structures to dramatically enhance the performance of the ceramic electrolytes used for high-temperature solid oxide fuel cells. Recent studies on nanocomposites of alternating layers of CaF₂ and BaF₂ show a linear increase in ionic conductivity (fluoride ion) parallel to the interface when the layers are 50 and 430 nm thick [20]. Space-charge calculations indicate that the increase is proportional to the interface density. However, a disproportionate increase in conductivity is observed when the alternating layers are narrower (16 to 50 nm thick). Under such conditions, the interfacial space-charge regions overlap, and the nanoscale layers lose their individual behaviors, taking on the properties of a super-ionic-conducting material possessing anomalous transport properties [20]. Similar enhancements in ionic transport (and electronic transport) may be possible with other ceramics, opening up exciting opportunities for nano-architecturing of future fuel-cell electrolytes.

Opinions, interpretations, conclusions, and recommendations are those of the authors and are not necessarily endorsed by the Office of Naval Research or the Naval Research Laboratory.

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Dr. Karen Swider-Lyons is a staff scientist in the Chemistry Division at the Naval Research Laboratory in Washington DC. She studied Chemistry as an undergraduate at Haverford College and earned her Ph.D. in Materials Science and Engineering from the University of Pennsylvania in 1992. Her research is dedicated to power sources, with a focus on the study of transport mechanisms in solid state ionic materials. She currently does research and development of microbattery systems and in new oxide-based catalysts for use in polymer exchange membrane fuel cells. She also serves as a technical consultant on two DARPA fuel cell programs. Dr. Swider-Lyons is a member of the Materials Research Society, the Electrochemical Society, and the International Society for Solid State Ionics.

Material

E A S E



Richard Lane, Benjamin Craig and Wade Babcock
AMPTIAC, Rome, NY

MATERIALS ENGINEERING WITH NATURE'S BUILDING BLOCKS

This article provides a brief overview of the major events, science, tools and processes in nanotechnology. Part One highlights the history of nanotechnology, Part Two discusses the tools used to study such small-scale materials and the underlying mechanisms responsible for the novel properties observed, and Part Three covers the major processing methods of nanomaterials.

Part One: History of Nano Materials Engineering

Nanotechnology is definitely one of the most talked about "new" areas of study today. The idea that nanostructured materials would exhibit unique properties is accredited to Gleiter and Turnbull for the work they did independently in the early 1980s [1]. Since then the field of nanotechnology has expanded dramatically due to the realization of its potential technological benefits.

Nanotechnology basically is the process of manipulating matter at the atomic scale. There are many interpretations of what this includes, but for our purposes and our inherent focus on materials engineering, we will include the purposeful creation, manipulation and machining of engineered materials at the nanoscale. Typically, nanomaterials have some critical dimension more than 1 and less than 100 nanometers, where a nanometer is one billionth of a meter, or one thousandth of a micron. The typical "yardstick" at small scales - a human hair - is about 200,000 nanometers in diameter. (A more thorough description of nanoscale is included in Part Two.)

Humans have been utilizing nanomaterials for centuries, dating back to Roman potters and possibly before. Ancient craftspeople utilized nanoscale particles in glazes to create unique colors that changed with incident lighting. In the 19th century, the use of metals in new and astounding structural applications drove the importance of microstructure to the front of engineers' minds. With this focus, empirical methodologies for processing metals yielded massive improvements in strength, toughness, ductility and hardness. Much of this work was microtechnology, even before the field existed, and one could argue that it bordered on the nano regime with the empirical manipulation of microstructure, precipitates and crystallographic grains.

Eventually, innovations such as the automobile demanded more durable consumables like rubber, glass, and ultimately, plastics. Rubber may have been the first modern example of nanotechnology, with the addition of carbon black and sulfur to improve durability. Even though the ability of engineers to study the exact mechanisms at work did not exist, carbon black's nanoscale particles served to modify the behavior of rubbers, thus assisting the growth of one of the most important manufacturing booms of the late 19th and early 20th centuries. While nanotechnology claims its roots in chemistry, the fields of physics and engineering have joined the fray and are pushing the boundaries of the possible.

Many trace the roots of modern nanotechnology and nanomaterials to a 1959 talk given by Dr. Richard Feynman at a meeting of the American Physical Society.* It was in this now-famous lecture that Feynman proposed the all-too-

simple hypothesis that there was "plenty of room at the bottom." He speculated that future scientists and engineers would build complex structures from atoms and molecules.

It wasn't until 1974 that the field was given the name "nanotechnology" however, and that is widely attributed to University of Tokyo researcher Norio Taniguchi. He made the distinction between engineering at the micrometer scale (the basis for modern microelectronics that was just starting to hit its stride in the 70s) and the new field of sub-micrometer engineering that was beginning to emerge†[2]. Nascent nanotechnology began to "grow up" and enter the mainstream consciousness in the mid-1980s with work by Richard Smalley at Rice University on what would be called Buckminster Fullerenes (now famously known as "Buckyballs") and MIT researcher K. Eric Drexler's publication of "The Engines of Creation."

While Smalley tantalized chemists and physicists with the discovery of a "new" form of one of the building blocks of nature, Drexler outlined a future dominated by a new form of manufacturing done at the molecular, and even atomic level. The study of Buckyballs has led to the discovery of tube-like structures of carbon atoms which are basically sheets of graphite rolled up with their edges connected to form a cylinder. They can be thousands of times longer than they are in diameter. It is these carbon nanotubes (CNTs) which have piqued the interest of so many engineers as they may hold the promise of extremely high tensile strength inclusions for nanocomposites, structural beams for nanomachines, and possibly even conductors (wires) for nanoelectronics. CNTs and other molecular-level structures form the bases of what Drexler describes as a coming revolution in molecular manufacturing.

What is most amazing about the development of micro- and then nanotechnology is the pace at which it has advanced. Taniguchi predicted in 1974 that within 15 years there would be machining methods capable of sub-100 nm dimensional precision. This prediction was largely proven correct. By the early 1990s, nanotechnology's capabilities could not only image and probe atomic structures, but move individual atoms, one at a time, around on a substrate. The "quantum stadium" image generated by IBM researchers provides a poignant example of this in Figure 1. The image consists of 76 iron atoms on a copper substrate. Wave patterns in the interior are from the density distribution of trapped electrons.

Since 1990, significant advancements have been made, both in actual materials fabrication and in computational simulation. The manufacturing of CNTs and many other nanomaterials has been improved and scaled up,

Material E A S E

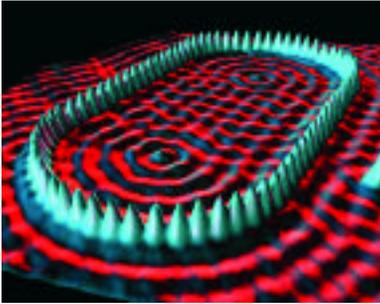


Figure 1. Quantum Stadium
(Courtesy: IBM, Almaden
Research Center. All rights reserved)

making affordable materials available for test and evaluation which did not exist just 5 years ago. Computer power has improved dramatically over the past 10 to 15 years, enabling atom-level simulation of many new nanomaterials before significant resources are invested in producing them. Researchers are now able to theorize, simulate,

manufacture, test, and evaluate new materials in much shorter times, further expanding the field and reducing wasted effort. While many of the ideas surrounding engineering at the atomic and molecular level are still in a highly speculative stage, experts agree that there seem to be no physical laws barring further advances.

Many of the advancements in nanotechnology were made possible by concurrent advancements in analysis tools capable of resolving atomic, molecular and crystallographic structures. Just in the last 20 years, various forms of scanning probe microscopy (SPM) and transmission electron microscopy (TEM) have become available to researchers on a reliable basis. These tools, described more fully in Part Two, have provided views into the inner workings of atomic bonding, molecular assembly, and the structure of materials at the smallest scales in history. It is these tools that have taken atomic manipulation out of the chemistry beaker and into the realm of engineering.

Part Two: The How and Why of Nanotechnology A Sense of Scale

To grasp what nanotechnology encompasses, it is critical to have a mental concept of what “nano” really means. Roger Whatmore of Cranfield University in the UK provides an excellent example in which he proposes that one imagine a human hair is roughly the size of a large tree trunk, one meter across. Now a typical bacterium (1 micrometer) would be about as big as a caterpillar on that tree and a typical virus (which is about 100 nanometers long) would be the size of an ant. And that is where nanotechnology is just getting started. Figure 2 presents an overview of items from the macro to the nanoscale. One can see that multiple technical disciplines of chemistry, physics, engineering, biology and others converge as we approach the lower reaches of size.

Analysis and Tools

In order to study materials on the nanoscale, instruments capable of very fine resolution must be utilized. Many of the microscopy tools used for characterizing nanostructures can easily fit inside a shoebox. Advances in microscope probe tip technologies have come about from the study of nanostructured materials, creating even better tools for characterization. Figure 3 compares some microscopy techniques and illustrates the incredible recent growth of tools with micro- and then nanoscale resolution.

Scanning Probe Microscopy One of the first tools used for nanomaterials investigation was the scanning tunneling microscope, or STM, developed by Gerd Binnig and Heinrich Röhler at IBM in 1981. (They would win a Nobel Prize in 1986 for this work.) The STM formed the basis for what would later become a family of scanning probe tools, or scanning probe microscopy (SPM), the key features of which are depicted in Figure 4.

Scanning probe microscopes use an atomically “sharp” tip (typically pyramidal in shape and coming to a point that is literally one or two atoms across) which is moved over a sample’s surface a few Angstroms from making contact. The tip is then scanned across the surface in a regular pattern (much as one would mow a lawn) and the electrical current, which traverses the gap between the tip and the sample, is monitored. By keeping the height of the tip constant and measuring the changing electrical current (more when close to the sample, less when farther away), or by keeping the current constant and measuring the deflection of the tip, a topographical map can be generated of the sample’s surface. The device relies upon the small amount of electric current which crosses the gap between the tip and the sample (“tunneling”).

The other most widely used member of the SPM family is the atomic force microscope or AFM. Similar to the STM, it uses an atomically sharp tip, but instead of carefully moving it just Angstroms from the sample, the AFM actually drags its tip along the sample’s surface. (This exaggerates the interaction at this scale - the atomic forces actually prevent atoms from “dragging,” they simply are pushed into very close proximity.) The tip is mounted on a cantilever

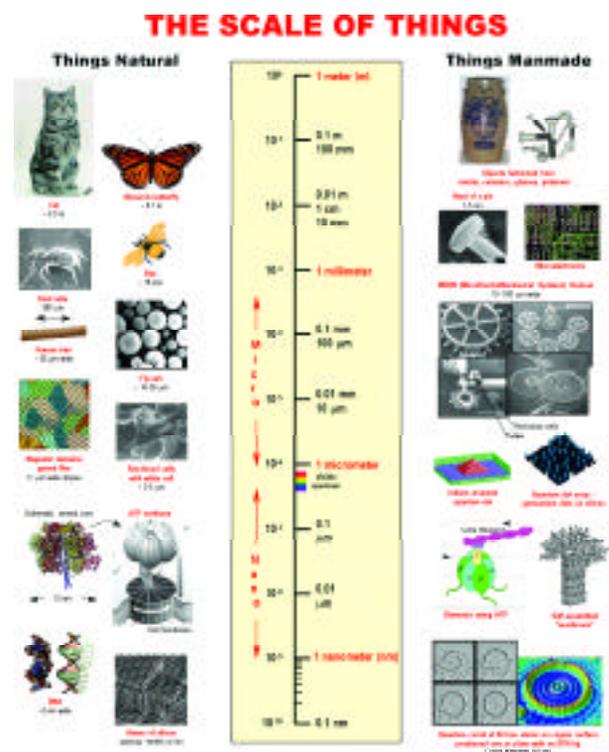


Figure 2. Scale of Common Natural and Manmade Items
(Reprinted with permission of the Office of Basic Energy Sciences,
Office of Science, US Department of Energy)

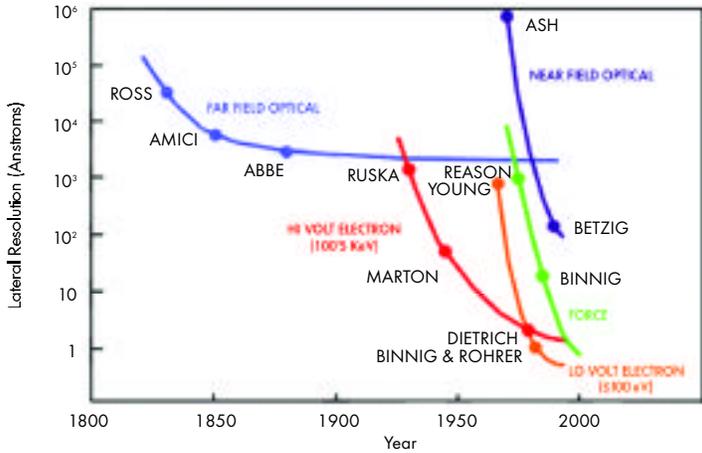


Figure 3: History of Lateral Resolution in Microscopy
(Courtesy of J. Murday, Naval Research Laboratory)

which flexes as the tip moves up and down the surface topography. Its deflections can be tracked by bouncing a laser beam off the cantilever into a split photodiode or by other techniques.

Magnetic Force Microscopy (MFM) is another technique of SPM, but uses a magnetic probe to sense the magnetic field above the surface of a material. The probe is standard silicon- or silicon nitride-coated with a thin magnetic film, such as cobalt, capable of mapping the magnetic domain of a specimen with a resolution up to 20 nm. Two passes are required to distinguish the topography of the sample. The first pass is in contact or semicontact with the sample and the second pass is at a specific constant height above the first pass.

Electron microscopes have been instrumental in the study and characterization of materials since the invention of the first electron microscope in the 1930s. High resolution transmission electron microscopy can now provide structural characterization at better than 0.2 nm spatial resolution. In its simplest form, a TEM consists of an electron beam that is projected through a thin sample, generating a diffraction pattern onto a receiving device, such as a phosphorescent screen or CCD camera. At low resolution, amplitude contrast images are used to map material structures in the 0.5 nm to 1 mm range. Specimens must be < 10 nm thick to provide the highest resolution

Nanoscience

The promise of nanotechnology is based upon the ability to create nanostructured materials that will produce novel properties on the macroscale. That ability now exists, however in many cases the mechanisms behind these observed properties are not yet clearly understood. Despite this incomplete understanding, it is still possible to attribute, by inference, the novel qualities of these nanomaterials to the following changes in internal structure.

1. The increased total surface area of grains, as grain size is decreased, will alter the physical properties of nanomaterials.
2. The increased volume of grain boundaries relative to unit structure, as grain size is decreased, will alter the physical properties of nanomaterials.
3. Discrete electronic levels (quantum behavior) will alter the electrical and optical properties of nanomaterials as grain sizes approach the molecular scale. The discrete energies associated with electron orbits become more evident as grain size nears the molecular scale (approximately < 5 nm), creating non-linear property effects.

Mechanical Properties The most widely accepted hypothesis to explain the mechanical properties in polycrystalline nanomaterials is that the strength and hardness follow the Hall-Petch relationship, increasing with smaller grain size, down to a critical grain size, $d_c \approx 10$ nm, where a decrease in strength and hardness results thereafter, as depicted in Figure 5 [3].

The increase in strength is based upon the piling up of dislocations at grain boundaries; i.e. by increasing the total surface area of grains, the dislocation density increases and in turn increases strength. However, pileups cannot occur when the grain size is less than the dislocation spacing in the pileup [4]; and so the Hall-Petch relationship will no longer be valid on this scale. The strength of nanoscale-thickness, multi-layered materials also follows the Hall-Petch relationship, replacing grain size with layer thickness.

By decreasing grain size, the grain boundary volume relative to the unit volume will increase. At roughly 5 nm, 50% of the volume will be grain boundaries [5], which may then dominate the properties observed in the material. The decrease in strength at this small end of the nanoscale may be attributed to grain boundary sliding due to the high defect density allowing fast diffusion of atoms and vacancies in the stress field [6]. Superplasticity [+] has been observed in nanostructured metals and ceramics at about 200°C lower than microstructured materials. This creates improved formability of nanostructured materials, which is especially important for ceramics.

Thermal Properties The enhanced diffusivity observed in the grain boundary structure of nanostructured materials is the mechanism thought responsible for the changes in thermal properties. In metals, thermal conductivity and melting point have been observed to decrease (such as a 27°C lower melting point for gold) while thermal expansion coefficients have been observed to increase. The decrease in thermal conductivity of nanostructured ceramic materials such as yttria stabilized zirconia may broaden their use as thermal barrier coatings.

Chemical Reactivity An increased chemical activity can be obtained by the large number of atoms on the surface of nanocrystallites providing active sites for reactions. For instance, nonstoichiometric CeO_{2-x} has a high chemical reactivity resulting from an unusually high oxygen vacancy concentration [7]. Nanostructured CeO_{2-x} has been demonstrated to offer catalytic activation for SO_2 reduction and CO oxidation at significantly lower temperatures as well as enhanced poisoning resistance (resistance to the loss of catalytic reactivity).

A second class of reactive materials are nanostructured porous materials. Conventional porous materials such as aluminosilicates and phosphates are

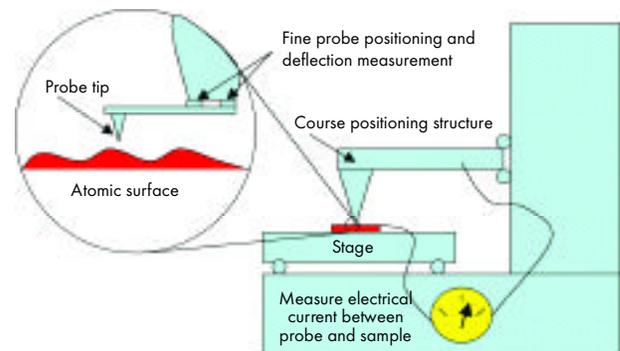


Figure 4: Graphical Depiction of the Key Features of an SPM

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used for catalytic reactions and gas absorption applications, but they are limited due to their small pore sizes of less than 15 Å [8]. Nanostructured aluminosilicates with optimized pore sizes in the range of 20–100 Å have been developed which extend their use in these markets. Similar research is being applied to the use of transition metal oxides in petrochemical production, pollution control, and pharmaceutical and fine chemical synthesis. Extending the pore sizes beyond the 20–100 Å range could provide benefits for enzyme catalysis, bioseparation and biosensing.

Optical Properties The size of dispersion materials in a composite can alter the wavelength of light that is absorbed by the particulates. The quantum effect is responsible here where the discrete electron energies in the particulates determine the wavelength of light absorbed. Altering the size of a particle can change the associated energy and wavelength of light absorbed. Cadmium selenide is one material extensively studied where crystallites of ~ 1.5 nm will appear yellow, 4 nm will appear red, and larger particles will appear black [9]. This discovery is now being applied to sunscreen lotions using zinc oxide and titania to filter ultraviolet radiation.

Electrical Properties Quantum effects in nanomaterials have been shown to produce a non-linear dependence of electrical conductivity on electric field and can produce electron tunneling characteristics. Quantum mechanical interference between separate paths an electron may take through a material can strongly enhance or suppress electrical conductivity. Most of the research to date in nanostructured electronic devices comes from fabrication via lithography, but inroads are being made into molecular-level structures fabricated from chemical reactions or self assembly. For instance, quantum dots are pyramid- or faceted dome-shaped clusters of atoms, typically between a few nanometers and hundreds of nanometers in diameter. They self-assemble from the deposition of a large lattice constant material onto a substrate with a small lattice constant, whereby the compressive strain in the deposited material relieves itself by causing the material to spontaneously coalesce or clump into islands on the substrate. They may be utilized as three-dimensional potential wells if they are overgrown by a material with a larger bandgap and have applica-

tion potential in nanoelectronics. (See the article in this issue by Dr. Amirtharaj et al for further information and application of quantum dots.)

CNTs (the tubes formed from rolled up sheets made of carbon atoms joined in hexagonal arrays) have shown some interesting electrical properties as well. The way in which the two ends of the sheet wrap and meet can modify the longitudinal conductivity of the tube. In fact, they can be made to conduct freely like metals or behave like semiconductors. And further advancements have shown that various-sized tubes can be nested inside one another for structural or electrical performance modifications.

Magnetic Properties Magnetic nanoparticles exhibit unusual behaviors resulting from the size effects and charge transfer characteristics. Changes seen in these materials include Giant Magneto-Resistance (GMR) in some layered composite materials and granular solids, spin valves, and spin injection in ferromagnet/insulator/ferromagnet sandwich materials.

Part Three: Processing of Nanomaterials

Bulk Methods

A number of processes are used for producing nanomaterials in bulk powders, coatings, thin films, laminates, and composites. However, there are two fundamental approaches to fabricating nanomaterials. The “bottom-up” approach represents the concept of constructing a nanomaterial from basic building blocks, such as atoms or molecules. This approach illustrates the possibility of creating exact materials – materials that are designed to have exactly the properties desired. The second approach, the “top-down” method, involves restructuring a bulk material in order to create a nanostructure.

INERT GAS CONDENSATION Considered a “bottom-up” method, inert gas condensation (IGC) was the first method used to intentionally produce a nanostructured material, and has become widespread. It can be used to produce nanostructured metals, alloys, intermetallics, ceramic oxides, and composites. The process begins by energizing a source material, which generates a vapor of atoms. This evaporation process can be performed through electron beam heating, laser ablation, sputtering, or plasma methods, but is most often done through Joule-heating. Due to condensation, the vaporized atoms agglomerate and form very small clusters when they are introduced to the inert gas. These

clusters are carried by a convection current, induced by thermophoresis, to a tube cooled by liquid nitrogen where they accumulate.

Adjusting certain parameters, such as the gas used (i.e. He, Ar, Kr, Xe), the gas pressure, the precursor evaporation rate, and the residence time, allows some control over the particle size and distribution. The smallest particle sizes produced using this method are about 5–25 nm using a precursor with a low evaporation rate

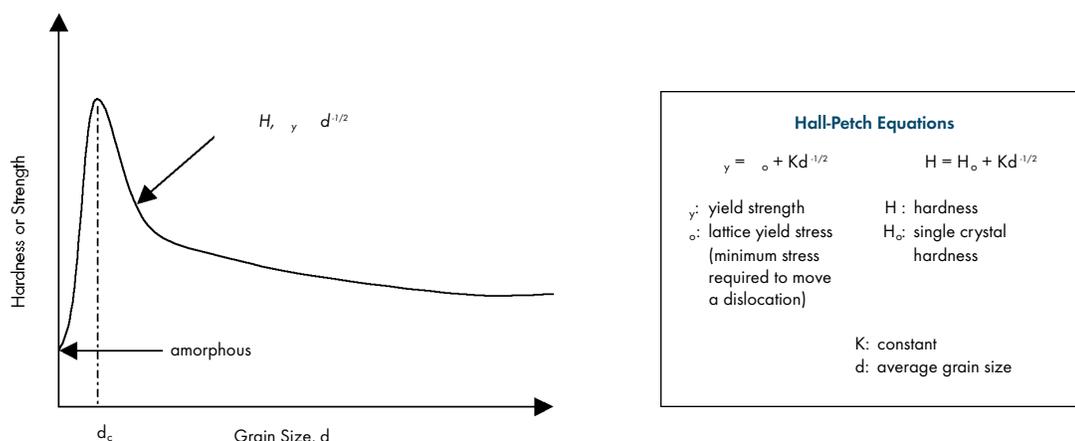


Figure 5: Strength/Hardness of Nanostructured Materials [3]

and a light inert gas at low pressure [10]. Since the process takes place in ultra-high vacuum systems (UHV), there is very little contamination of the material, and therefore, it remains highly pure.

MECHANICAL ALLOYING Another process commonly used to produce nanostructured materials is mechanical alloying, which is an example of a "top-down" method. There are two basic versions of this process. The first, more specifically called mechanical attrition, is a process where high-energy ball milling is used to grind and refine the structure to produce highly mixed, ultra-fine powders. Grain sizes of the material are partially dependent on time, where extended milling times result in more uniform grain sizes. The second version, reaction milling, involves in-situ solid-state chemical reactions between precursor materials while they are mixed and milled.

Producing large quantities of nanostructured material is one advantage of the mechanical alloying process. Moreover, various types of nanomaterials, such as metals, ceramics, intermetallics and composites, can be produced using these straightforward processes. However, contamination from the milling hardware and environment, non-uniform particle sizes due to short milling times, and non-homogeneous chemical composition due to incomplete milling reactions are problems for mechanical alloying processes. One way to lessen the effects of environmental contamination is to perform the process in the presence of liquid nitrogen, which is also referred to as cryogenic milling.

SEVERE PLASTIC DEFORMATION Severe plastic deformation (SPD) is used to fabricate nanocrystalline metals and intermetallics. There are several different types of SPD processes, but the three most common processes are equal-channel-angular extrusion (ECAE), torsional straining and accumulative roll-bonding (ARB) [10]. Nanosized grains are created when the material is subjected to a very large deformation causing a modification of its structure by fragmenting the existing phases. Recrystallization of these broken phases results in structures with significantly reduced sizes. The materials formed by SPD generally have average grain sizes of about 100 nm, although grain sizes down to 20 nm have been obtained for metals [11]. The grain size controlling parameters in this process include temperature, strain, strain rate, and applied pressure. Severe plastic deformation is capable of forming nanostructured materials with little contamination and little or no porosity. A further advantage is that SPD is a scalable process, meaning that it could be used for industrial applications. However, since there is significant straining of the material, high residual stresses may be present in the end product.

SOL-GEL The sol-gel method is a solution phase processing technique that is used more often to fabricate nanostructured materials than any other liquid phase process. This is a process capable of producing nanostructured ceramics and nanocomposites. There are essentially two phases present during this technique, where one is a homogeneous solution phase and the other is an elastic, gel-like, solid phase. The homogeneous solution is dried, thereby transforming it into a gel, while maintaining a constant volume. Subsequent drying causes a phase transformation of the gel along with a corresponding reduction in volume, ultimately resulting in the desired phase. The key to obtaining a nanostructured material using this process is to control the processing parameters. One advantage to solution phase processing is the excellent control it provides over the chemical composition, which leads to a more homogeneous composition [10]. A disadvantage to this process is that the starting materials can be expensive.

Coating and Laminate Methods

Nanostructure coatings have been primarily deposited via thermal spraying. Processes used to fabricate laminates include: Radio Frequency sputtering, DC magnetron sputtering, chemical vapor deposition, electroplating, and physical vapor deposition methods including electron beam, cathodic arc, and jet vapor deposition [12].

THERMAL SPRAYING Thermal spraying is a process capable of producing nanostructured materials and nanostructured coatings. Control over the composition and structure of the final material is very important when producing nanostructured materials, and for this reason powders are typically used as the starting materials. The powders are carried by a gas (i.e. air, N₂) and heated such that they are at least partially melted. Deposition onto a substrate results in the deformation and solidification of the particles.

ELECTRODEPOSITION Electrodeposition has traditionally been used as a coating process, although recently it has also been used to form bulk nanocrystalline materials. This process is capable of producing a nanocrystalline material with grain sizes down to 5 nm. The factors affecting the resulting grain sizes include pH, temperature, current density, and type of current among others [10]. The process can be carried out at room temperature and the time of fabrication is of course dependent on the size of the material to be produced. For example, as one would expect, larger materials take longer, but compared to other deposition processes, electrodeposition is capable of rapid deposition. Moreover, electrodeposition is a less expensive process that can be used for large-scale production [10].

JET VAPOR DEPOSITION Jet vapor deposition is a relatively cost-effective technique capable of rapidly depositing multilayered films with alternating material layers to produce a nanostructured composite [13]. Nanostructured multilayered films consist of layers with nanoscale thickness. Sonic or nearly sonic gas jets, typically helium, carry an atomized material and deposit it as a film on a substrate. Uniform deposition occurs with a rotating or oscillating substrate which is mounted on a carousel. Alloys and multilayered composites are formed by employing two or more jets simultaneously or in sequence, respectively. An optimum deposition temperature needs to be maintained to ensure minimal interdiffusion between the layers and a continuous nature of the layers without impurities forming in between.

SPUTTERING Sputtering is a well-known and widely used technique for producing thin films. It is a vacuum method capable of producing nanostructured materials. In this technique, plasma, which is generated by energizing a low-pressure gas such as argon, strikes a target transferring its momentum which causes the target material to be ejected and subsequently deposited onto a substrate. The main disadvantage to the sputtering method is that it is difficult to control. DC-magnetron sputtering and RF-diode sputtering have been used to prepare nanolaminate materials. These methods are capable of depositing layers of a material with a thickness below 100 nm.

CHEMICAL VAPOR DEPOSITION The process of chemical vapor deposition (CVD) involves a gas-phase chemical reaction which forms a solid material on a substrate. Nanostructured ceramics and composites are the most common types of nanomaterials produced by CVD (Carbon nanotubes are also fabricated using CVD). Vapors of the precursor materials are transported by a carrier gas to a heated substrate where they are deposited and subsequently react with the substrate to form a solid material. Although it is a relatively slow process, chemical vapor deposition offers good control over the chemical

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composition and is capable of deposition over a large area. There are several variations of the CVD process, such as plasma assisted CVD and laser assisted CVD.

CHEMICAL VAPOR INFILTRATION Chemical vapor infiltration (CVI) is a technique that is used to form nanostructured fiber-reinforced composite materials. A very similar process to CVD, CVI uses a transporting gas to carry vaporous precursors to a porous fiber preform, while diffusion takes the precursors inside where they react and form the nanostructured matrix. An important issue with CVI is ensuring that the outer parts of the fiber preform are not sealed off prior to the interior being fully deposited. To prevent premature surface densification, the chemical vapor infiltration process is slowed by adjusting the process parameters, such as temperature, pressure, and reactant concentration. Another factor to CVI being a slow process is that it is limited by the diffusion mechanism of the gaseous precursors. The advantage to CVI is that it is capable of producing a fiber-reinforced composite without damaging the fibers, which is often a problem in other composite processes.

CHEMICAL VAPOR CONDENSATION Another chemical vapor process used to produce nanomaterials is chemical vapor condensation (CVC). A precursor vapor carried by a gas stream is sent through a heated (hot-wall) reactor tube, where the pyrolysis of the precursor occurs to form nanoparticles. The nanoparticles are then collected on a liquid-nitrogen cooled tube. The CVC process is a low-pressure technique that requires a low concentration of the precursor in the carrier gas stream. Process parameters such as temperature, pressure, and residence time can be adjusted to determine the size of the nanoparticles. A variation of this process is the combustion flame version which replaces the hot-wall reactor with a combustion flame reactor. The combustion flame reactor supplies a significantly higher temperature which increases the reaction rate.

For further coverage of the subject matter, the interested reader can find more information on nanostructured materials in "Nanomaterials: Synthesis, Properties and Applications" [14].

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† Norio Taniguchi shows the trend in ultraprecision machining from 1900 and projects that it will reach "Atomic lattice distance" (0.3 nanometers) around 2017.

+ Superplasticity is the ability of a material to exhibit large ductility, usually > 200%.

Nanoceramic Coatings Exhibit Much Higher Toughness and Wear Resistance than Conventional Coatings

*Dr. Lawrence T. Kabacoff
Materials Science and Technology Division
Office of Naval Research*

Introduction

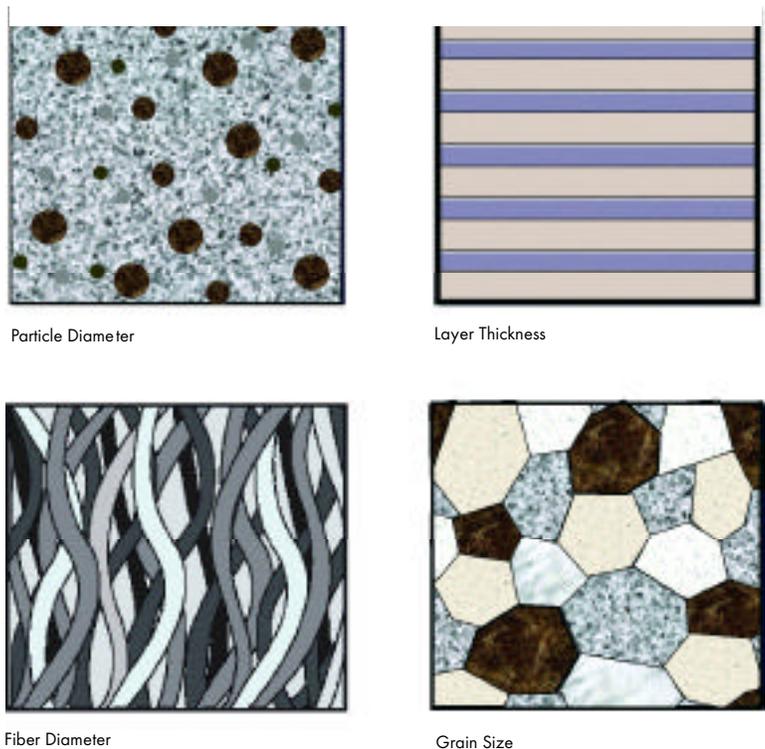
Modifying material surfaces to enhance wear and corrosion resistance is a common practice for both military and commercial applications. Electrodeposited hard chrome is one of the most widely used protective coatings. Ceramic coatings, both single phase and composite types, are also common and they are frequently applied using plasma spray. In this process, the coating material (usually in the form of a powder) is injected into a plasma stream where it is heated and accelerated toward the substrate surface. After impacting the surface the ceramic rapidly cools thus forming a coating layer.

Both hard chrome and ceramic coatings have serious deficiencies that can limit their use. Chrome electroplating uses closely regulated hazardous materials. Compliance with the various environmental safety regulations has made hard chrome increasingly expensive to use. Plasma-sprayed ceramic coatings are somewhat less expensive than chrome (when clean up costs are included), but are generally brittle and have limited success adhering to substrates, which is also a problem for hard chrome. The need for better coating materials has been recognized and considerable effort has recently gone into finding replacements.

Over the last five years, a consortium of companies, universities and Navy personnel have been developing a new generation of wear resistant “nanostructured” ceramic coatings. The consortium is led by Inframat, Inc. and the University of Connecticut, and team members include the A&A Company, Rutgers University, Stevens Institute of Technology, the Naval Surface Warfare Center (Carderock Division) and Puget Sound Naval Shipyard. It is funded by the Office of Naval Research and its objective has been to achieve mechanical and wear properties unobtainable from more conventional materials (i.e. materials with structural aspects at the micron scale or larger).

Nanostructured materials are characterized by an ultra-fine microstructure with some physical aspect less than 100 nanometers in size. This feature can be grain size, particle or fiber diameter, or layer thickness (Figure 1). There are two reasons why reducing the scale of a material’s microstructure can significantly alter its properties. First, as grain size gets smaller, the proportion of atoms at grain boundaries or on surfaces increases rapidly. In a polycrystalline material with a grain size of 10nm, as many as 50% of its atoms are at grain boundaries, resulting in a material with properties far different than nor-

Figure 1. Nanostructured Materials are Characterized by the Inclusion of One or More Types of Features with Dimension Below 100 Nanometers



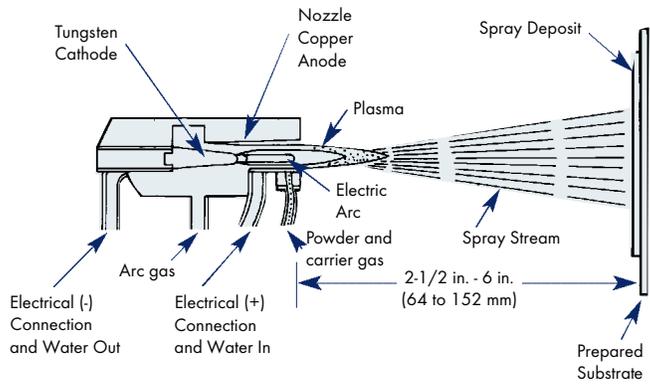


Figure 2. Schematic Diagram of Typical Plasma Torch (Courtesy of R.W. Rigney)

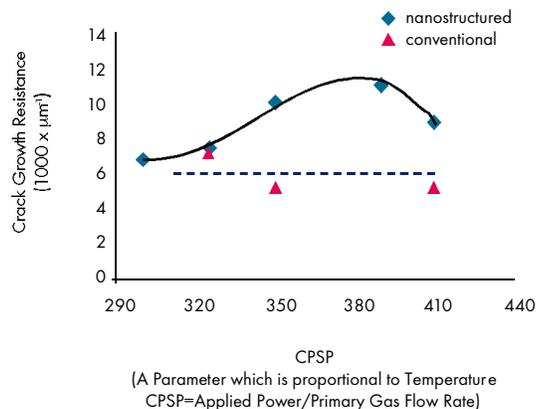


Figure 3. Indentation Crack Growth Resistance vs. Critical Plasma Spray Parameter (proportional to plasma temperature) [3]

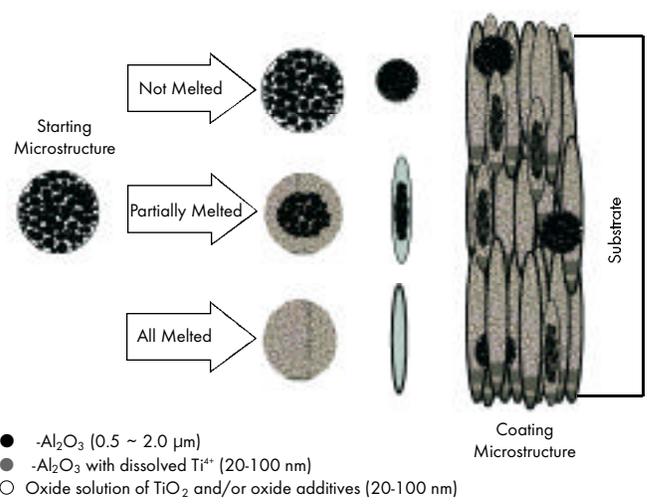
mally seen. The other reason is related to the fact that many physical phenomena (such as dislocation generation, ferromagnetism, or quantum confinement effects) are governed by a characteristic length. As the physical scale of the material falls below this length, properties change radically. Until recently, these changes in deformation behavior and modes of failure have not been well understood due to the inability to consistently fabricate high quality materials. This situation is changing rapidly, with considerable progress now being made in the fabrication of nanomaterials, as well as and the understanding of the interrelations between nanoscale processing, structure, and macroscale properties.

Fabrication of Nanoceramic Coatings

The strategy employed to develop nanostructured coatings concentrated on compositions similar to currently available conventional coatings and to use existing deposition equipment to fabricate them. As only the microstructure of the coatings was changed, it greatly simplified the process of implementing the new technology in both military and commercial applications. One of the coatings under development, a plasma sprayed nanoceramic composite with a composition of $Al_2O_3 - 13 TiO_2$, has exhibited wear resistance, bond strength, and toughness unprecedented in a ceramic, and is now in use aboard Navy surface ships and submarines, reducing maintenance costs due to wear and corrosion.

Plasma spray, the process used to fabricate ceramic coatings, is very simple in concept, but very complex in practice. An inert gas is passed through a region of electrical discharge, where it is heated to very high temperature (typically 10,000 to 20,000 K). The rapidly expanding plasma is forced out through a nozzle at velocities between 1,200 and 1,500 m/sec and directed toward a substrate. Particles are injected into the plasma, where they are heated and accelerated. Although the plasma and particle temperatures are high, substrate surface heating is minimal. A schematic of a typical plasma spray gun is shown in Figure 2. The complexity arises from the large number of parameters that must be selected and which can affect the structure and properties of the coating. The temperature and velocity of the plasma depend on the power applied to the gun and the type and flow rate of the gas used. Usually, two gasses are used, an inert gas such as helium or argon, and a secondary gas, such as hydrogen. Other factors include the morphology of the powder particles, distance from the gun to the substrate, position and orientation of the powder injection ports, and surface preparation of the substrate. Taken all together, these

Figure 4. Effect of Nanoparticle Agglomerate Melting on Coating Microstructure [3]



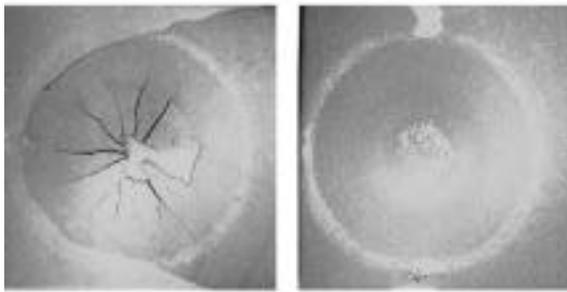


Figure 5. Cup Test Performed on Conventional (Left) and Nanostructured (Right) Al_2O_3 - 13TiO_2 Coatings (Courtesy of R.W. Rigney)

parameters determine the thermal history of the injected particles, velocity of impact, and flow and solidification characteristics after impact, thus dictating the resultant microstructure.

As compared to traditional plasma spray processes, plasma spraying nanostructured materials introduces a number of complications. The first is that nanoparticles cannot be sprayed by particle injection into the plasma. Very small particles lack the momentum necessary to penetrate into the plasma, or to impact the surface while the plasma sweeps to the side near the substrate. To be sprayed, the particles must be formed into agglomerates approximately 30-100 microns in diameter. For an Al_2O_3 - TiO_2 nanocomposite, this is usually accomplished by dispersing alumina and titania nanoparticles in a fluid with a binder and spray drying [1]. If necessary, the agglomerates are partially sintered to improve structural integrity.

The next problem is forming a nanostructured coating on the substrate. This is not trivial since the agglomerates are greatly heated (promoting rapid grain growth) and are at least partially melted. There are three mechanisms for creating or retaining a nanoscale microstructure: avoiding melting or grain

growth of the feedstock (very difficult), inclusion of nanoscale particles with very high melting temperature that remain solid while the rest of the material melts, or formation of a nanostructure during solidification of the sprayed material upon impact. The last mechanism occurs in composites consisting of two or more immiscible phases (as is the case for Al_2O_3 and TiO_2) and results from solid state decomposition of a single, metastable phase formed by rapid solidification during impact. The metastable phase formed by Al_2O_3 and TiO_2 is a highly defected Spinel [2].

The microstructure and properties of nanostructured Al_2O_3 - 13TiO_2 coatings depend strongly on the temperature of the plasma [3]. This is in sharp contrast to the conventional coating, as illustrated in Figure 3, which shows a plot of indentation crack resistance as a function of a parameter (applied power divided by primary gas flow rate) which is proportional to the plasma temperature. Data is shown for both the nanostructured and conventional coatings. One can see that the crack growth resistance for the conventional material is virtually independent of plasma temperature while the nanostructured coating exhibits a strong dependence.

The reason can be found by following the thermal history of the injected particles. In the plasma spraying of conventional Al_2O_3 - 13TiO_2 , the feedstock consists of large fused and crushed particles that are fully melted prior to impact. Full melting is achieved over a wide range of temperature because of the high thermal conductivity of fused and crushed particles (relative to nanoparticle agglomerates). The coatings typically have grain sizes greater than one micron. When the nanoparticle agglomerates are sprayed at relatively high temperature (under conditions that result in full melting), the “nano” structure consists entirely of grains formed from the decomposition of the metastable Spinel phase.

The difference between the micro-grained material formed from fused and crushed feedstock and the nanostructure formed from the agglomerates arises from the degree of homogeneity in the melted particles. Because of the short residence time, the liq-

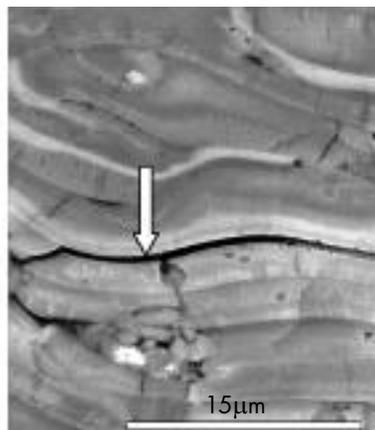
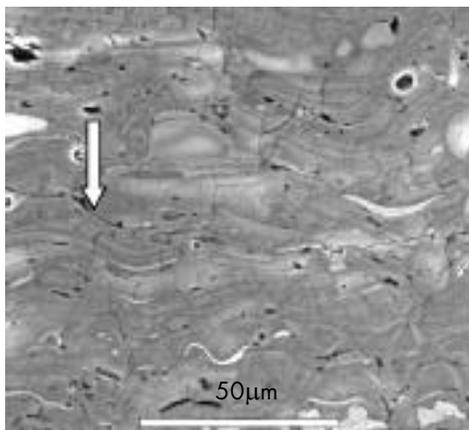


Figure 6. Cross-Sectional Views of Crack Propagating in Conventional Al_2O_3 - 13TiO_2 Coating [3]

liquid formed from melting the fused and crushed particles will contain alumina and titania rich regions. When this liquid solidifies rapidly, the grains formed will be larger than would be obtained from a homogeneous liquid. When plasma spray is carried out at a relatively low temperature, little melting occurs and the structure consists of incompletely sintered particles that have undergone some degree of grain growth. The middle temperature range gives partial melting of the agglomerates and results in regions of micron sized grains (from unmelted particles that have experienced grain growth) surrounded by nanoscale grains from the fully melted material and is illustrated in Figure 4. It is this “duplex” structure that gives the best properties, not a homogeneous nanoscale structure.

Properties of Nanostructured Al_2O_3 - 13TiO_2 Coatings

The obvious parameter by which to judge a “wear resistant coating” is wear rate. Wear can be termed as either sliding or abrasive. Both are measured by running a “wearing” medium over the surface and measuring weight loss. For many coatings, and particularly for brittle materials such as ceramics, this parameter can be misleading. The wear resistance of coatings in use today is outstanding, with wear rates orders of magnitude less than the uncoated surface. Brittle coatings usually do not fail by “wearing out”, but rather suffer from cracking, delamination and spallation. At least as important as wear resistance is bond strength (adhesion to the substrate) and toughness (the ability to withstand an impact or applied strain). It is in these properties that the nanoceramic coatings excel to a remarkable degree.

The bond strength of the nanostructured coatings, as measured by tensile pull tests on coatings applied without a bond coat, is about double that of a conventional coating. The toughness of the nanostructured Al_2O_3 - 13TiO_2 coatings is extraordinary, as is dramatically illustrated in Figure 5. This shows a “cup test” in which a coated coupon is forced down onto a one-inch diameter steel ball (coated side away from the ball), causing it to deform. The deformation is greatest in the center decreasing to zero at the edges. The conventional coat-

ing shows the typical cracking and spalling observed in a ceramic. The nanostructured coating actually deforms along with the substrate and no macroscopic cracking is observed. A blow from a hammer severe enough to deform a steel substrate would not be sufficient to cause failure in the coating. This toughness translates into greater wear resistance, which is two to four times greater than that of the conventional coating [4].

Another important benefit of enhanced coating toughness is improved grindability as almost all ceramic coatings must be ground and polished after spray deposition. Nanostructured ceramic coatings can be ground and polished in about half the time required for conventional ceramic coatings. Since grinding and polishing operations represent about forty percent of the total cost of the coating (compared to about five percent for the cost of the feedstock powder), nanostructured coatings are actually less expensive to apply.

The performance of the conventional and nanostructured coatings can be better understood by examining how cracks propagate in these materials. In the conventional coating, cracks follow the “splat boundaries” which mark the borders between the materials deposited from each droplet (Figure 6). The arrows in this figure point towards a splat boundary. A crack can be seen following another splat boundary [3]. In the nanoceramic composite, the cracks do not follow the splat boundaries, but instead propagate through the nanostructured material that formed during solidification until they encounter a region of larger grains formed from partially melted feedstock. Here, the cracks are either deflected or stop inside the “coarse grained” region. This can be clearly seen in Figure 7, which illustrates that cracks terminate inside regions (see arrows) of large grains formed from unmelted feedstock [3]. Any strain imposed upon a nanostructured coating is accommodated by the creation of microcracks in the normal way, but these cracks are blunted before they can propagate very far or link up with other cracks. The result is a ceramic material that can deform to a degree much greater than in a more conventional, brittle ceramic.

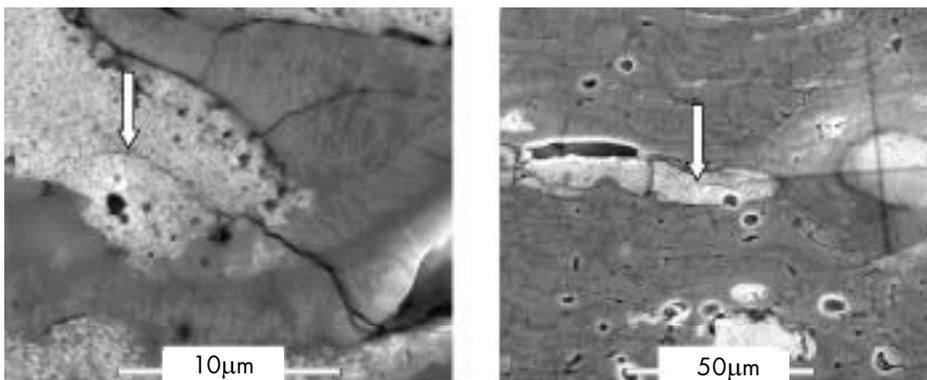
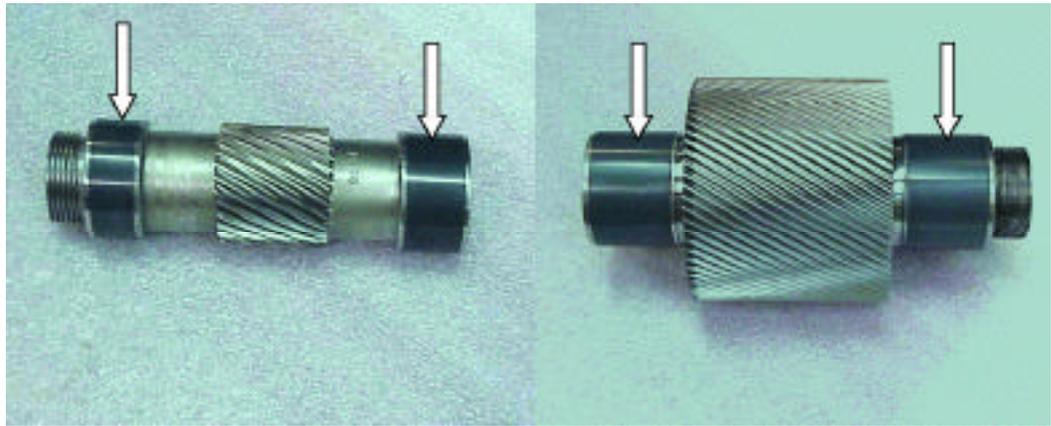


Figure 7. Cross-Sectional Views of Crack Propagating in Nanostructured Al_2O_3 - 13TiO_2 Coating With “Duplex Structure” [3]

Figure 8. High Speed Reduction Gear Set From 80 Ton Air Conditioning Unit. Coated Areas are Marked with an Arrow (Courtesy of R.W. Rigney)



Applications

The applications for nanostructured $\text{Al}_2\text{O}_3 - 13\text{TiO}_2$ coatings can be grouped according to the properties to be exploited. The simplest applications are those in which the nanostructured coatings replace existing conventional ceramic coatings. In such cases, the advantage is greater longevity and reliability. The second case is as a replacement for hard chrome coatings. Here, the advantages are lower cost, elimination of toxic hazardous materials and in some cases, improved performance. The improved performance comes from the non-metallic nature of ceramics. Metallic surfaces in contact with seawater for long periods of time experience buildup of calcareous deposits. Actuator rods with such buildups can severely damage seal areas when the rods are retracted. Electrically non-conducting coatings experience no such buildup. Also ceramics do not promote galvanic corrosion, which occurs when two dissimilar metals are in contact with an electrical conductor such as seawater. In spite of these advantages, conventional ceramic coatings frequently cannot be used over metallic coatings because they lack sufficient bond strength and toughness. Nanostructured ceramics overcome this limitation. In fact, nanostructured $\text{Al}_2\text{O}_3 - 13\text{TiO}_2$ coatings are now being used to coat titanium components on seawater-exposed portions of submarines specifically to eliminate galvanic corrosion on nearby steel structures. The most unique applications are in circumstances where no coatings could previously be employed. For example, many shafts used aboard ships, such as propulsion shafts, undergo sufficient torsional strain to cause failure in a conventional coating. Nanostructured $\text{Al}_2\text{O}_3 - 13\text{TiO}_2$ coatings exhibit sufficient strain tolerance to be a viable candidate for coating of severe wear areas on certain types of shafts.

The qualification of a new material for military applications can be a fairly involved process. This process has been greatly simplified for nanostructured $\text{Al}_2\text{O}_3 - 13\text{TiO}_2$ coatings because the coatings are similar in composition to existing approved coat-

ings and are applied using the same equipment and procedures. They have now been approved under MIL STD 1687A, which governs use of thermal spray coatings on shipboard machinery. The number of applications in use aboard surface ships and submarines is rapidly expanding. There are literally thousands of potential applications and the impact on the cost of maintaining ships, aircraft, and ground vehicles can be very large. This can be demonstrated by examining a typical example.

The component illustrated in Figure 8 is a reduction gear set from an 80-ton air conditioning unit used on surface ships. The coated areas of these gears are indicated by the arrows. Currently gears are replaced on average at six year intervals. Eventually, abrasives form on the shaft, excess heat is generated and it welds to the aluminum sleeve in which it rotates, thus causing it to seize up. With application of the new coatings, these gears can be repaired instead of replaced. The damaged surface is ground down and replaced with a nanostructured $\text{Al}_2\text{O}_3 - 13\text{TiO}_2$. The savings fleet-wide from this one application is about \$500,000 per year, or about \$13,000,000 over the projected thirty-year life of these ships. When one considers the large number of other applications, such as pumps, valves, electric motors, diesel engines, bearings, journals and actuators, the magnitude of the cost savings becomes apparent. Moreover, most of these components are not military-specific. Coatings are now being applied to commercial hardware as well.

While nanostructured ceramic particles and thin films have been available for some time, nanostructured $\text{Al}_2\text{O}_3 - 13\text{TiO}_2$ represents the first bulk ceramic material to be commercialized. Other nanostructured coating materials are under development and are expected to become available in the near future. These include cemented carbides, such as Tungsten Carbide-Cobalt (WC-Co) and other ceramics, such as chrome oxide and yttria-stabilized zirconia. All of these coatings are expected to find a wide range of application and should greatly benefit both military and commercial operating and maintenance costs.

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Nanoenergetics: An Emerging Technology Area of National Importance

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Introduction

Energetic materials are a major component of weapons systems used by all branches of the US military. Their primary use is in explosives, as well as in gun and missile propulsion. Over the last century new chemicals have been discovered or designed for rapid release of energy in either relatively simple compositions, like that used in certain warheads, or in more complex formulations like the advanced composites used as propellants. Currently, a class of energetic materials known as nitramines are actually used for both explosives and propulsion applications in various weapons systems. Some major considerations for successful weaponization of energetic materials include performance (e.g. energy density, rate of energy release), long-term storage stability, and sensitivity to unwanted initiation.

As demands on munitions increase with regards to improved performance (i.e. increased lethality and survivability as well as the development of emerging high precision weapons concepts), the challenge on the R&D community is ever increasing. Additional drivers and concerns for the US military come from the continuing development of new munitions (including new types of energetics) by foreign nations. Munitions development is also fundamentally impacted by the approaching limit of the amount of improvement that is possible for the traditional and now rather mature C, H, N, and O energetic chemistries.

In recent years researchers have found that energetic materials/ingredients that are produced on the nanoscale have the promise of increased performance in a variety of ways including sensitivity, stability, energy release, and mechanical properties. As such, they represent a completely new frontier for energetic material research and development with the potential for major payoffs in weapons systems. Very simply, nanoenergetics can store higher amounts of energy than conventional energetic materials and one can use them in unprecedented ways to tailor the release of this energy so as to maximize the lethality of the weapons. The field of nanoenergetics R&D is quite young, but is already undergoing rapid growth. The goal of this article is to give the reader a sense for the physical and chemical characteristics and properties that make these materials so promising. This

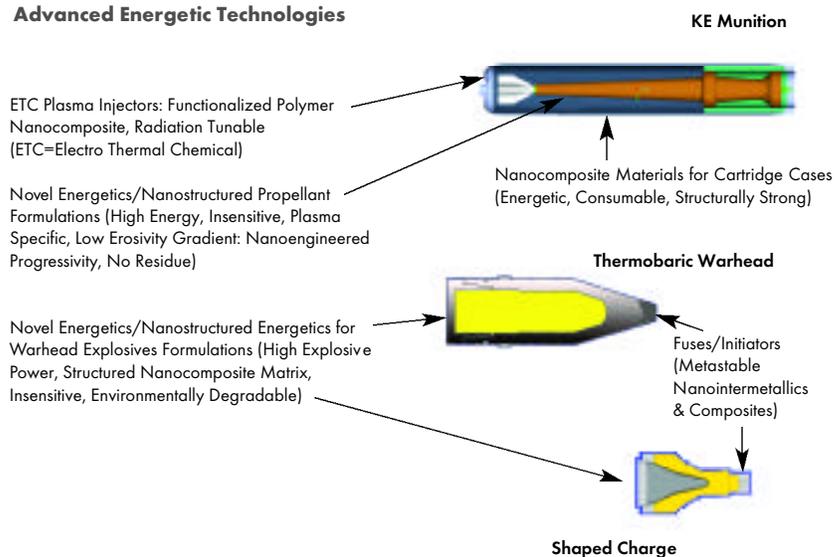
will be accomplished through a discussion of a few selected examples of current research.

Background

The 221st National Meeting of the American Chemical Society held during April 2001 in San Diego featured a symposium on *Defense Applications of Nanomaterials*. One of the 4 sessions was titled Nanoenergetics. This session featured speakers from government labs (DOD and DOE) and academia (for further information about this symposium, please contact the author). This session provided a good representation of the breadth of work ongoing in this field, which is roughly 10 years old. A number of topics were covered, including a few that will be discussed in detail below, namely Metastable Intermolecular Composites (MICs), sol-gels, and structural nanomaterials. The presentations given at this symposium largely form the basis for this report.

At this point in time, all of the military services and some DOE and academic laboratories have active R&D programs aimed at exploiting the unique properties of nanomaterials that have potential to be used in energetic formulations for advanced explosives and propellant applications. Figure 1 represents some concepts of how nanomaterials, especially

Figure 1. Weaponization of Advanced Energetic Technologies



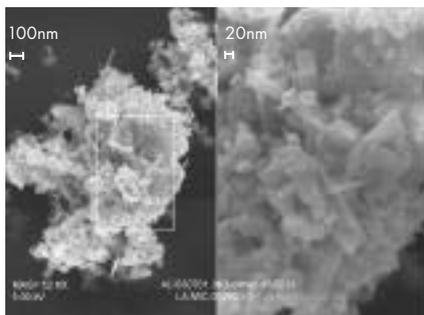


Figure 2. SEM of MIC (Al/MoO₃ Mixture)

nanoenergetics could be used for improving components of munitions. The figure shows that nanoenergetic composites and ingredients can be used in the ignition, propulsion, as well as the warhead part of the weapon. With regards to the latter application, nanoenergetics hold promise as useful ingredients for the thermobaric (TBX) and TBX-like weapons, particularly due to their high degree of tailorability with regards to energy release and impulse management.

Metastable Intermolecular Composites (MICs)

Metastable Intermolecular Composites (MICs) are one of the first examples of a category of nanoscale energetic materials which have been studied and evaluated to a considerable degree. MIC formulations are mixtures of nanoscale powders of reactants that exhibit thermite (high exothermicity) behavior. As such, they differ fundamentally from more traditional energetics where the reactivity is based on intramolecular (not intermolecular) properties. The MIC formulations are based on intimate mixing of the reactants on the nanometer length scale, with typical particle sizes in the tens of nanometers range (e.g. 30 nm). One important characteristic of MICs is the fact that the rate of energy release can be tailored by varying the size of the components. Three specific MIC formulations have received considerable attention to date; Al/MoO₃, Al/Teflon, and Al/CuO.

Research and development on MIC formulations is being performed in laboratories within all military services, as well as at Los Alamos National Laboratory (LANL). LANL researchers Drs. Wayne Danen and Steve Son, along with their colleagues, have not only pioneered the dynamic gas condensation method for the production of nanoscale aluminum powders (also known as Ultra Fine Grain [UFG]), but they have also conducted numerous studies on physical and chemical properties. As an example, Figure 2 shows a scanning electron microscope (SEM) image of a nanoscale MIC (Al/MoO₃ mixture) produced by the dynamic gas condensation process at LANL. One

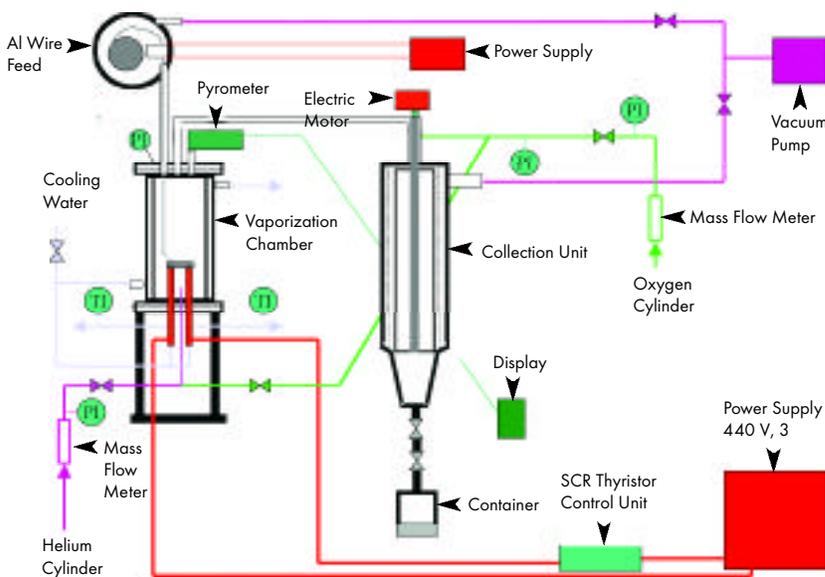


Figure 3. The Process Schematic for the Production of Nanoscale Al for MIC Applications at NSWC/Indian Head

critical aspect of producing successful MIC formulations is the ability to produce nanoscale aluminum particles of small particle sizes in the tens of nanometer range, as well as with reasonably narrow size distribution. And, of course, the production process needs to be reproducible batch to batch. The current state of UFG aluminum production is that this is an area that still requires considerable effort. Even though there are commercial sources for UFG aluminum (such as the ALEX process originated in Russia, or commercial sources in other nations such as Japan), the need for reliable non-government sources of ingredient materials for uses in MIC applications is still there. Progress in this area is being made by companies such as Technanogy and Nanotechnology.

Another example of a significant effort at producing MIC compounds is found at the Indian Head Division of the Naval Surface Warfare Center (NSWC/IH). This work is being performed by Dr. Magdy Bichay, Pam Carpenter, and Tom Devendorf along with other co-workers. The Indian Head process for producing UFG aluminum is also based on the dynamic gas condensation process with some changes, such as the use of resistance heating instead of RF coils. Figure 3 shows

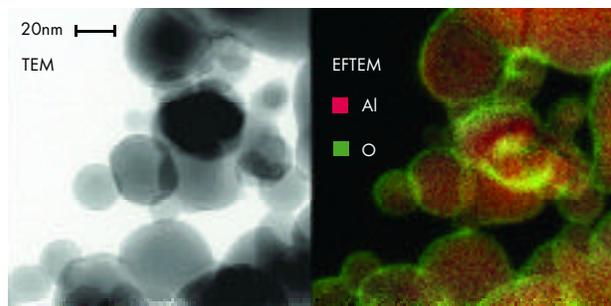


Figure 4. Al Nanoparticles with a Passivation Layer of Al₂O₃

the process schematic as developed by Professor Jan Puszynski of the South Dakota School of Mines, working in concert with Indian Head. Design goals included the use of continuous aluminum wire feed, a continuous collection system, as well as a production rate of approximately 10 grams/hour. It was found that one major limitation of the process was the 12 hour life of the titanium diboride/boron nitride ceramic resistance boat used for heating the material.

Figure 4 shows an example of the typical UFG aluminum that is produced by the Indian Head process. A transmission electron microscope (TEM) image of the Al nanoparticles is shown on the left while an EFTEM (energy filtered TEM) is shown on the right, clearly indicating a thin passivation layer of Al_2O_3 . These images were taken at Lawrence Livermore National Laboratory (LLNL). In summary, much more research and development needs to be done in the production and characterization of these and new types of MIC formulations. Issues of MIC ignition and safety characteristics (such as impact, friction, and electrostatic initiation) are promising, but need to be fully explored. Overall though, certain key MIC characteristics are very attractive and quite promising for practical applications. These include energy output that is 2x that of typical high explosives, the ability to tune the reactive power (10 KW/cc to 10 GW/cc), tunable reaction front velocities of 0.1-1500 meters/sec, and reaction zone temperature exceeding 3000K. Specific areas of possible applications include use in environmentally clean primers and detonators, chem/bio agent neutralization, improved rocket propellants, IR flares/decoys, thermal batteries, and others.

Sol-Gels

Researchers at LLNL, Drs. Randall Simpson, Alexander Gash, et al., have pioneered the use of the sol-gel method as a new way of making nanostructured composite energetic materials. The advantages of making energetics on the nanoscale are shown in Figure 5 which provides a comparison between conventional energetic compounds (micron scale) and those which are composed of nanoscale ingredients. The sol-gel chemistry involves the reactions of chemicals in solution to produce primary nanoparticles, called “sols”, which can be linked in a 3-dimensional solid network, called a “gel”, with the open pores being occupied by the remaining solution. There are typically two types of sol-gels. “Xerogels” are the result of a controlled evaporation of the remaining solution/liquid phase, yielding a dense, porous solid. On the other hand, “aerogels” can be formed by supercritical extraction (SCE), which eliminates the liquid surface tension and thus alters the capillary forces of the egressing liquid that normally would lead to pore collapse. Since the pores have been largely kept intact through the use of the SCE method, the resulting solid is highly porous and lightweight, with excellent uniformity given that the particles and the pores are both in the nanometer range. Figure 6 illustrates the sol-gel methodology.

The sol-gel approach is fundamentally different than most approaches to energetic material production in that it is a relatively simple methodology (e.g. chemistry in a beaker) performed at low temperatures. It can also be relatively inexpensive

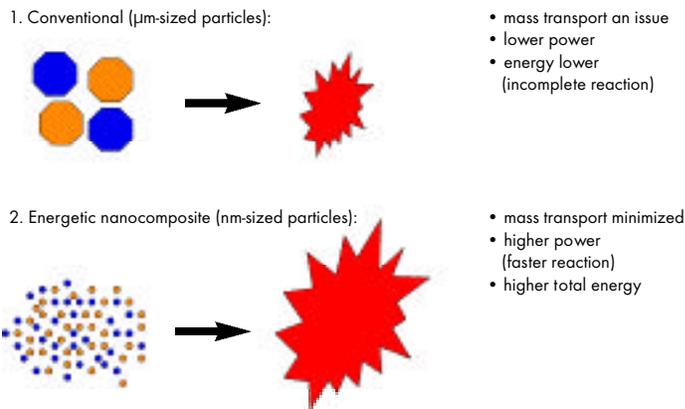


Figure 5. Composite Energetic Materials: Conventional vs Nanosized

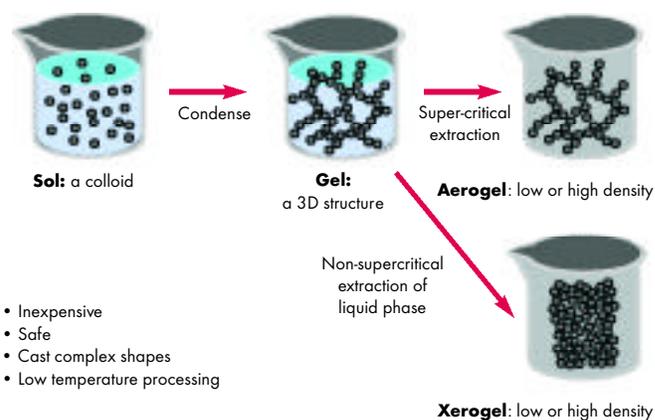


Figure 6. The Sol-Gel Methodology

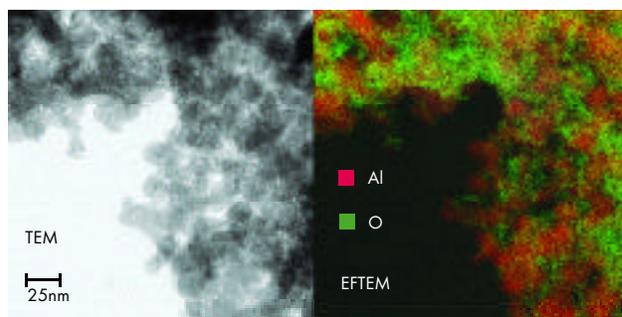


Figure 7. Sol-Gel $\text{Fe}_2\text{O}_3/\text{Al}$ Nanocomposite

and has the promise of creating entirely new energetic materials with desirable properties.

One current promising nanocomposite being pursued by the researchers at LLNL involves the use of Fe_2O_3 which is generated using the sol-gel method. The reason that Fe_2O_3 is chosen is because its thermite reaction with UFG aluminum is very exothermic (with only CuO and MoO_3 yielding greater energy of reaction). An example of the high degree of mixing and uni-

Figure 8. The Coiled Graphitic Structure of Carbon Nanotubes



Figure 9. Micrograph of Amine-Terminated Carbon Nanotubes



formity between two nanophases is found in Figure 7, which indicates the excellent dispersion of Al and Fe on the nanoscale domain. The Fe_2O_3 was prepared by the use of an organic epoxide which was added to an Fe(III) salt solution resulting in the formation of nanoscale crystalline and amorphous Fe_2O_3 . The reaction to produce Fe_2O_3 was done in solution which already contained the UFG aluminum. In this case, the nanoparticle aluminum was sonicated (suspended in isopropanol and placed in an ultrasonic bath to break up any aluminum aggregates) before mixing with the Fe(III) salt solution. For this work, the UFG aluminum was supplied by the NSWRC researchers at Indian Head using the dynamic gas-phase condensation method (discussed above), which yielded an average aluminum particle size of approximately 35 nanometers.

As sol-gel materials and methodology advances, there are a number of possible application areas that are envisioned. These include: (1) high temperature stable, non-detonable gas generators, (2) adaptable flares, (3) primers, and (4) high-power, high-energy composite explosives. In addition, the sol-gel chemistry may have advantages of being more environmentally acceptable compared to some other methods of producing energetics.

Functionalized Carbon Nanotubes for Energetic Applications

Dr. Lalitha Ramaswamy and her colleagues at the University of Maryland, along with Army Research Laboratory scientists (Drs. Matt Bratcher, Pamela Kaste, and Sam Trevino) are exploring the use of carbon nanotube structures (Figure 8) as starting material for various possible energetics applications. One concept involves the functionalization of carbon nanotubes with the notion of incorporating or binding this material into propellant matrices. The hope is that by doing so there will be significant performance enhancement in the areas of initiation, overall propellant performance, safety, as well as in mechanical properties. One specific goal that is being pursued is the assessment of carbon nanotube-based ingredients for the improvement of propellant initiation for either an advanced plasma-based initiator (which is under development), or for use with more conventional electrical initiators. Here the optical as well as electrical properties of nanotubes may be important in

generating an improved propellant formulation. In particular, the high electron density that characterizes the nanotube structure as well as the high conductance along the tube wall may lead to more robust and reliable ignition behavior.

Long-term storage stability is one of the key elements of a successful propellant formulation. In this regard, there is hope that carbon nanotubes could be used to encapsulate nanoscale energetic ingredients, perhaps even the nitro-organic energetic compounds themselves (e.g. HMX, RDX), to yield a propellant that not only has the same (or better) performance for energy release, but also much improved performance for handling and long-term storage. An example of progress in the effort to functionalize carbon nanotubes is given in Figure 9 which shows a micrograph of some amine-terminated carbon nanotubes. In addition to the synthesis of functionalized carbon nanotubes this effort also involves chemical analyses of the products as well as the use of characterization techniques such as Prompt Gamma Activation Analysis for elemental ratio analyses.

Center for NanoEnergetics Research at the University of Minnesota

One of the major challenges that will be faced by the Department of Defense sometime in the near future (with regards to the utilization and implementation of nanoenergetic materials and ingredients) will be the ability to produce such materials in not only large quantities, but also in controlled sizes, size distributions, and chemical compositions. To address this eventuality, the DOD has recently funded a university-based research program in a competitive process through the Defense University Research Initiative on NanoTechnology (DURINT) program. This research program is headed by the University of Minnesota, which established the Center for NanoEnergetics Research (CNER) (see www.me.umn.edu/~mrz/cner.html). The primary goal of the CNER is to conduct a comprehensive and multidisciplinary study of the high rate production and behavior of nanoenergetics. Professor Michael Zachariah is the Director of the CNER and he has expertise in the synthesis and in-situ characterization of nanoparticles, as well as molecular dynamics simulations of particle growth and

production. A significant aspect of this DURINT-funded program is the close scientific collaboration with a DOD research organization, namely the Army Research Laboratory. ARL researchers Dr. Barrie Homan and the author of this article are working closely with Professors Zachariah and Steven Girshick and their research groups in developing virtually identical nanoenergetics production and characterization facilities. Figure 10 shows a schematic of this research facility which represents the centerpiece of the CNER. It is based primarily on the use of a thermal plasma arc reactor for the production of a large number of possible precursors in the solid, liquid and vapor phases. In addition to the plasma, provisions have been made for the use

of a furnace, as well as a diffusion flame apparatus, to serve as alternate techniques for producing nanoscale ingredients. In addition to the production of single or multicomponent (e.g. metals or multimetals) nanoscale particles, this facility allows for the in-situ coating of the particles using a number of different approaches (e.g. condensation or uv curing). This coating could be chosen to be an inert shield to keep the core nanoinredient from further reacting with air (oxygen or moisture), or it could be chosen to be energetic to dramatically increase the energy density of the final energetic formulation.

Characterizing the nanoenergetic particles produced in this facility is accomplished by two major diagnostic approaches. The first involves the use of a single particle mass spectrometer (SPMS, inset photo in Figure 10). Here the SPMS is used to provide size and elemental composition of the particles as they are sampled from the reactive flow. As such, this tool tracks the growth as well as the coating of the targeted nanoenergetic ingredients/composites. Nanoscale particles of different sizes are selected for analysis using aerodynamic focusing. These selected particles can also be analyzed in-situ using spectroscopy. Two techniques in particular are powerful tools for analyzing small particles; Laser Induced Breakdown Spectroscopy (LIBS) and Laser Induced Incandescence (LII). LII has been developed primarily by the combustion research community as a major tool for understanding the formation of combustion-generated particulate matter. This technique utilizes a pulsed laser to rapidly heat the small particles. By monitoring the rate of decay of the resulting incandescent radiation, one can extract particle size information, as the rate is related to the size of the particle. In order to get information on the chemical composition of the particles through the use of spectroscopy, it is necessary to use a different technique. LIBS is an emerging major new tool for the analysis of chemical composition (see <http://www.arl.army.mil/wmrd/LIBS>).

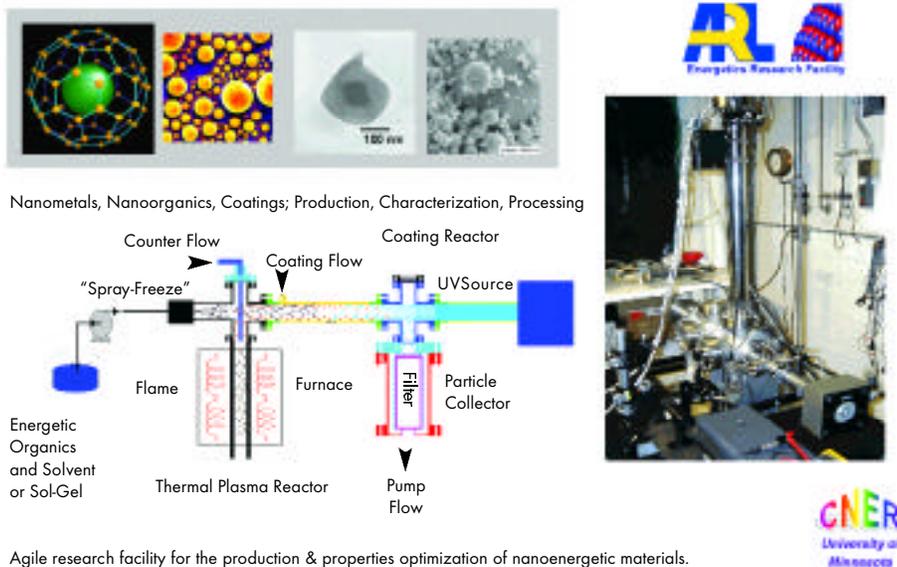


Figure 10. Schematic of Instrument to Produce Nanoscale Energetic Ingredients (Photo inset is the single particle mass spectrometer at the CNER- University of Minnesota)

In LIBS, a pulsed laser is tightly focused on the sample to induce a breakdown (microspark) of the sample material. The spark process leads to the breakup of the sample into its elemental components and simultaneous excitation of the resulting atoms and ions, which subsequently emit light. Thus, by monitoring the emission from this plasma, one can determine the nature of the element by its characteristic emission wavelength and the relative abundance by the intensity of the emitted light at a given wavelength. The LIBS sensor technology is advancing so rapidly that instrumentation has currently become available for the capture of light between 200-940 nm, a region where all elements emit. Thus, researchers are now in a position to simultaneously detect all of the constituent elements of nanoparticles, including the metals, carbides, and organic and/or oxide coatings. Since the LIBS data is generated in real-time (response time 1 second or less), one can keep track of rapid changes in the composition of the particles during the actual production run. Recently Professor David W. Hahn of the University of Florida has demonstrated LIBS analysis of nanoscale particles and has found that the LIBS technique can be very sensitive, having a resolution in the femtogram range (10^{-15} gm), and it is capable of detecting as few as 100 particles per cubic centimeter.

There are a number of other researchers and topics under the CNER umbrella. Professors Steven Girshick and Sean Garrick at the University of Minnesota are working on nucleation theory, aerosol dynamics, and the simulation of reactive flows while their colleague Prof. Alon McCormick, as well as Professor Tom Brill of the University of Delaware, are working on various aspects of sol-gel science. Other principal investigators include Professor Jan Puszynski of the South Dakota School of Mines who is working on solid-state chemistry and kinetics. On the theoretical side, Professors Don Thompson of Oklahoma State University and Don Truhlar of University of

Minnesota are working in the area of fundamental computations aimed towards the simulation of the behavior of nanocomposites. All in all, the CNER represents a major national resource for understanding the science and engineering as they relate to the generation and behavior of nanoenergetic compounds and ingredients. It should be mentioned that the Army Research Office (Drs. David Mann and Robert Shaw) had a major role in the selection of the DURINT topic on nanoenergetics and in the continued administration of the CNER contract which started in 2001 and could run through 2005.

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The Army Pushes the Boundaries of Sensor Performance Through Nanotechnology

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Sensors are not the first things that come to mind when considering the panorama of potential applications anticipated from the burgeoning field of nanoscience and nanotechnology. However, sensors are ubiquitous and play critical roles in the function of a wide range of electrical and electronic systems, from tiny electronic circuits to large and complex systems. For instance, electronic and optoelectronic circuits need voltage, current, temperature, light, and other sensors to operate. Jumbo jets need mechanical sensors and actuators to function. Nanotechnology offers hitherto unheard of possibilities in revolutionizing the sensors in use today and opening new frontiers in functionalities. To paraphrase Richard Feynman (please see this issue's MaterialEASE), *there is indeed still much room at the bottom* [1].

The Sensors and Electron Devices Directorate of the US Army Research Laboratory (ARL/SEDD), located in the Maryland suburbs of Washington, DC, is dedicated to the development of state-of-the-art sensors for our warfighters. We are actively pursuing avenues that take advantage of the exciting potential of nanosystems to improve on the current approaches, as well as look ahead to new sensor modalities. For example, we are harnessing the properties of semiconductor quantum-dots (QD) to improve infrared detection and are pursuing nanosize gold (Au) colloidal particles to enhance detection of biological threats. The advantages of nanoengineered materials are realized by harnessing the quantum properties observable in the nanoscale regime. Nanoscaled objects comprise the building blocks of the mesoscale world as we know it. However, our technology has only recently allowed us to design structures at this scale by having fundamental control over physical and chemical processes and molecular attributes.

ARL/SEDD has taken an integrated approach to developing sensors and advancing the underlying technology. For example, nanophase materials are grown and fabricated through techniques such as molecular beam epitaxy (MBE), yielding semiconductor quantum dots for infrared (IR) detectors. These materials are fabricated to produce functional devices which are then packaged and integrated into subsystems to produce fully functional prototype sensors. Substantial facilities, equipment and investments have been dedicated to the emerging field of nanosensors.

The Army has developed specialized tools to fabricate and analyze these tiny structures. One example is the magnetic resonance force microscope (MRFM), which is a scanning-probe-type instrument capable in some instances, of measuring the nuclear magnetic resonance (NMR) response of a single proton. Instead of detecting small electrical signals as conventional magnetic resonance imaging (MRI) does, MRFM detects atomic and subatomic forces mechanically. The instrument uses tiny magnets mounted on cantilevers fabricated using MEMS techniques. MRFM is several orders of magnitude more sensitive than conventional MRI for objects smaller than one-thousand cubic micrometers. Until recently, conventional electrically-detected MRI has lacked the sensitivity to make solids MRI useful, but MRFM will make force detected solids MRI a reality. (Note: Solids MRI differs significantly from medical MRI, which is a form of liquids MRI. This is because the human body is primarily composed of water, which provides an excellent NMR response to traditional magnetic resonance technology.) When perfected, MRFM should be able to image a single atom in a three dimensional (3-D), non-homogenous object. Such a breakthrough would find broad applications in biology, medicine, materials science, semiconductors, polymers, and many other areas.

Self-Assembled Quantum Dots for IR Detector Application

Molecular beam epitaxy (MBE) is a specialized, ultrahigh vacuum evaporation technique normally used to grow multilayer semiconductor films with interfaces that are essentially flat, even at the atomic level. However, if a material with a relatively large lattice constant were grown on top of a material with a smaller lattice constant, the large compressive strain energy could be relieved by spontaneous coalescence of the larger lattice constant material into 3-D 'islands' on the surface. These islands would take the form of crystallographic pyramids or multifaceted domes and could range in size from a few nanometers to several hundred nanometers. Because of their extremely small size and the manner in which they are formed, they are referred to as *self-assembled quantum dots*.

Figure 1 shows an atomic force micrograph of a set of InAs quantum dots grown on a GaAs substrate. The lateral dimensions are exaggerated because the radius of curvature of the

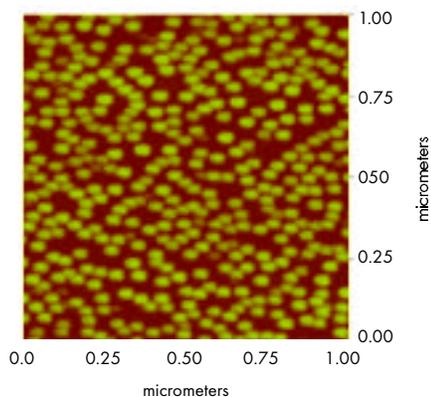


Figure 1. Atomic Force Micrograph of InAs Quantum Dots on a GaAs Substrate

probe tip is comparable to the size of the dots. If the islands are embedded in a host material with a larger bandgap (e.g., by crystal overgrowth of GaAs), they form isolated 3-D potential wells that have been shown to bind several discrete energy levels much like isolated atoms [2]. This is the 3-D analog to the one-dimensional (1-D) semiconductor quantum well that is formed when a very thin layer of a low-bandgap material is sandwiched between two higher-bandgap layers.

One of the results of carrier confinement in quantum wells is a strong infrared absorption that occurs when electrons in the ground state of the well (due to doping with electron donor impurities) are excited to a higher energy subband (allowed energy level within the conduction and valence “bands” of the quantum well). This effect has been used to make quantum well infrared photodetectors (QWIPs), which are the fundamental element of high-performance thermal imaging systems. Polarization selection rules for these intersubband transitions dictate that only light that is polarized in the direction of quantization (i.e., perpendicular to the quantum well layer) can be absorbed. Unfortunately, the typical geometry of a 2-D imaging array of QWIPs is such that light incident on the array has no polarization component perpendicular to the quantum well layers. This requires that each pixel of the array have a polarization rotating structure (typically a diffraction grating) etched into its surface, which limits the efficiency and producibility of QWIP detector arrays.

Since quantum dots confine carriers in all three dimensions, intersubband transitions can be excited by all polarizations of infrared light. Also, due to the discrete nature of the energy levels, the peak oscillator strength for normal-incidence infrared absorption should be very large in doped quantum dots. This suggests that quantum dots could be used to replace integrated optical coupling structures used in quantum well infrared detectors.

Figure 2 shows the polarization-dependent infrared photocurrent spectra of a quantum dot infrared photodetector (QDIP), consisting of a stack of InAs quantum dot layers separated by GaAs barrier layers. The QDIP responds to both polarizations of light in the wavelength range of interest for

thermal imaging. However, infrared detectors based on quantum dots are in their earliest stages of development. The dark currents are high, and it is difficult to predict the operating wavelength a priori because of the complexity of the structures. Researchers at ARL are currently conducting a systematic study of the interactions between the electronic levels of the quantum dots and the quasi-continuum of electronic states in the host (barrier) material surrounding them. Because of the wide range of semiconductor materials that are available for use in quantum dot systems and the flexibility and control of growth parameters offered by MBE techniques, rapid advances in the performance of infrared detectors based on self-assembled quantum dots will occur in the near future.

Nanotechnology for Displays and Biodetection

The Army has extensively investigated nanoscale structures to enhance the performance of a number of engineered material systems for a variety of sensor applications. Dendrimers have been examined as a means to encapsulate or capture chromophores and augment their physical and chemical properties. In other work, nanoscale structures and particles have been investigated for luminescent research that could have applications for future Army displays. Finally, nanostructures are being investigated for surface-enhanced Raman scattering in an attempt to detect and identify harmful biological agents in the environment.

Research and development of electronic materials form the foundation of the modern information revolution. As the dimensions of bulk solid-state devices rapidly approach the limits of processability, molecular-based devices that inherently take advantage of quantum physics will play increasingly important roles in electronic evolution. Organic semiconductors have demonstrated their potential as a new class of electronic materials for commercial applications including

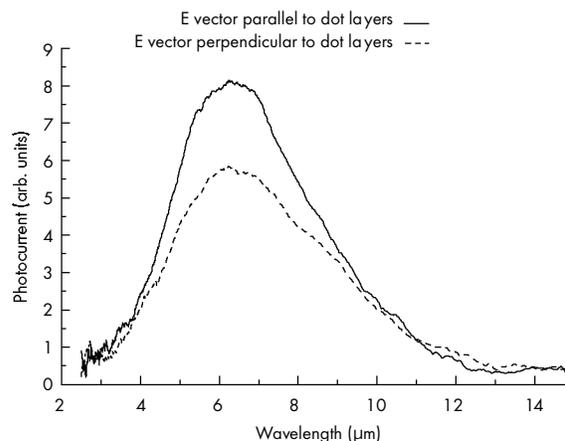


Figure 2. Photocurrent Spectra for an InAs/GaAs Quantum Dot Detector Structure (grown, fabricated, and tested at ARL) for Light Polarized Parallel and Perpendicular to the Quantum-dot Layers

electrophotography, light-emitting diodes (LEDs) [3], transistors [4], and sensors [5]. The pioneering work by Tang and Van Slyke [3] demonstrated that organic light-emitting devices (OLEDs) indeed have the necessary attributes and competitive advantages to be considered seriously for display applications.

An important distinction must be made between inorganic semiconductors and organic-based semiconductors. Inorganic semiconductors have occupied and unoccupied energy bands, valence, and conduction bands, respectively, that can extend over many unit cells. For typical Si-based semiconductors, these energy bands are determined by a tetrahedral bonding structure formed by sp^3 hybridization. For organic semiconductors, the occupied and unoccupied energy levels are formed from planar structures of sp^2 bonds as well as π -bonds. The combination of bonds form the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO), where the benzene ring is the typical bonding structure for most organic semiconductors.

For OLED applications, the organic films are typically not crystalline, which leads to a high degree of localization of the molecular orbitals on a single molecule. Thus, molecular-based electro-optical devices such as OLEDs rely on nanotechnology-

Cross-section of layered thin-film structure

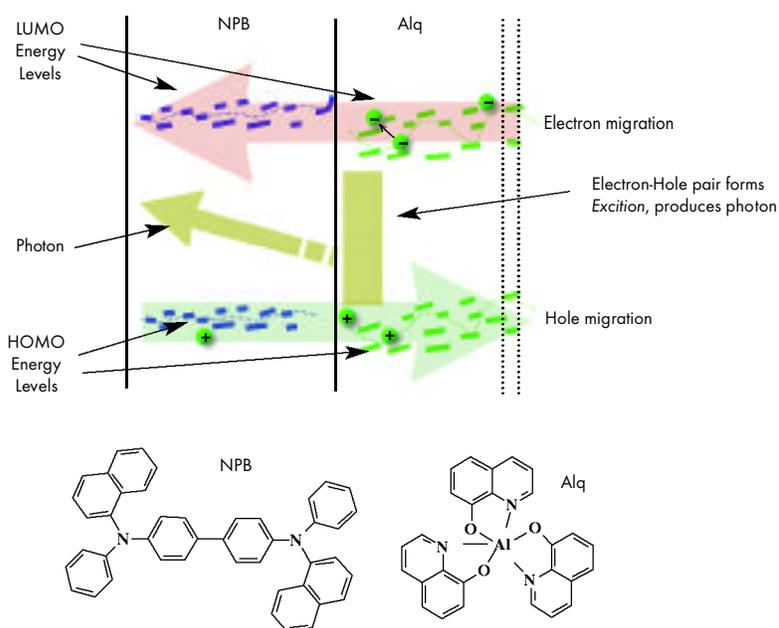


Figure 3. Energy Diagram for a Typical Small Molecule OLED

engineered materials that take advantage of quantum confinement at a molecular level. In OLEDs, the transport and light emission properties are limited by the injection and subsequent diffusion of hole and electron carriers from the anode and cathode, respectively, to the light emission region. The drift diffusion of holes and electrons is determined by a field-dependent hopping from a molecular orbital state that is energetically lower than the molecular state in a neighboring molecule.

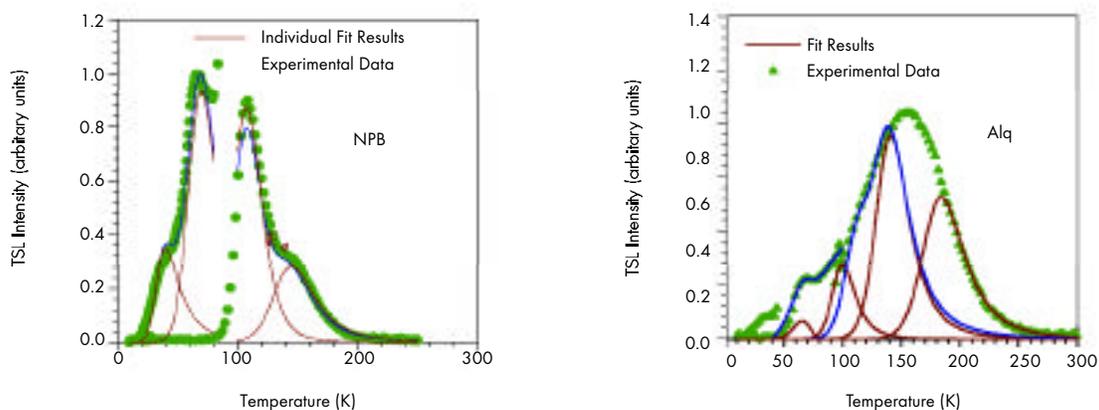


Figure 4. Thermally Stimulated Luminescence (TSL) Spectra for NPB and Alq. Results Show that the Energy Disorder (corresponding to temperature in the graphs) in Alq is Twice as Large as NPB. (The TSL for Alq occurs at a higher temperature than it does for NPB, thus the greater energy disorder.)

Then, an electron-hole pair combines on a single molecule, forming an exciton that ultimately decays with the emission of a photon.

Figure 3 displays an energy diagram for a typical small molecule OLED. The energetic disorder in molecular glassy films has been measured by the Army using thermally stimulated luminescence (TSL) [6]. These results show that the energy disorder is inherently larger in the electron-transporting tris-8 hydroxyquinoline aluminum (Alq) layer as compared to the hole-transporting N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1,1-biphenyl-4,4'-diamine (NPB) layer. This is in good agreement with the lower electron mobility in Alq as compared to NPB and can lead to an unbalanced carrier pair in the emissive region and device instabilities [7]. Figure 4 compares the TSL for NPB and Alq. In addition to organic-based displays, we are investigating inorganic nanoparticle-based emitters for display applications. As with organics, the quantum confinement in nanophosphors improves the recombination cross-section and light output efficiency.

Raman spectroscopy is an optical technique that provides information about the structure of molecules. It can be used in aqueous systems due to the weak Raman signal from water, making it ideal for analysis of biological organisms. Raman spectroscopy is inherently weak, but methods to enhance the signals have been known for over 25 years. Surface-enhanced Raman spectroscopy (SERS) requires nanometer-scale metal features to enhance the signals by up to 16 orders of magnitude. Army researchers are investigating several methods for preparing substrates with such nanoscopic features for the detection and identification of bacteria [8]. They include Au colloidal particles immobilized on surfaces, electrochemically roughened Au surfaces, and periodic particle arrays from Prof. Richard van Duyne at Northwestern University [9]. In each of these substrates, the feature size is in the 10 nm to 150 nm range. The degree of enhancement is strongly related to the size of the nanoscopic features and the excitation wavelength used.

The first critical step in collecting SERS spectra of bacteria is to develop an SERS substrate that the bacteria can approach within 10-100 nm. This distance requirement is established by the short range of the SERS enhancement. Since both a metal surface or particle and the bacterium have a negative surface charge, it is necessary to either modify the particle or surface with a small molecule to neutralize its charge or hold the surface at a neutral or slightly positive charge. The size of the enhancing features can then be optimized for the chosen excitation wavelength. Once the bacteria move within the SERS enhancement range, the spectra can be collected using laser excitation at 647.1 nm. Once a library of spectra is collected, advanced statistical analysis methods such as chemometrics or a neural network can be trained for the identification of the genus and species of the bacterium.

Nanoscale Electromechanical Systems (NEMS) for Radio frequency (RF) Filter Applications

ARL has a strong effort in piezoelectric microelectromechanical systems (MEMS) device fabrication, with specific expertise in lead zirconate titanate (PZT) based piezoelectric devices. These

include thin film resonators, magnetometers, vacuum pumps for chip-scale mass spectrometers, and power generation devices. PZT resonators with resonant frequencies from 0.2 to 9 MHz have been fabricated at ARL, and their response has been studied intensively [10]. Resonator arrays for RF filter devices operating in the GHz frequency range are of interest to the Army for lightweight, low-power, high-precision frequency selection applications, including wireless communication, tracking and surveillance, and weapons guidance and fusing. A high quality factor, or Q, is required in the resonator device to reduce phase noise and ensure stability against frequency-shifting phenomena [11].

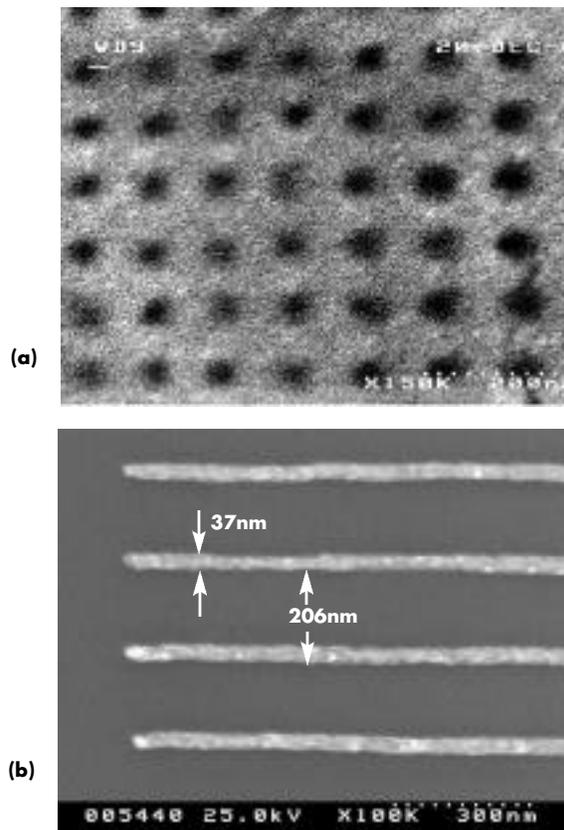
Electromechanical resonator devices offer potential advantages in size, weight, and power consumption over surface acoustic wave (SAW) or bulk acoustic resonators currently used for frequency filtering applications. Piezoelectric electromechanical resonator devices should demonstrate advantages over equivalent electrostatic devices for high-frequency applications, since they are less sensitive to degraded coupling strength as the device dimensions are reduced [12]. Equation 1 displays the Euler-Bernoulli beam equation for the natural resonance frequency of a doubly clamped mechanical resonating beam, where L is the length of the beam, t is the beam thickness, E is the elastic modulus, and ρ is the density [13].

$$\frac{\omega(L)}{2} = 1.027 \sqrt{\frac{E}{\rho}} \frac{t}{L^2} \quad \text{Eq. 1}$$

For resonance frequencies in the GHz range of interest, electromechanical resonator devices typically require lengths in the range of 1 to 10 mm, with thickness and width dimensions on the order of hundreds of nanometers. Material properties factor prominently in the frequency response. The roles of grain boundaries, defects, and other nonbulk materials characteristics of thin films are unknown at present and must be investigated to effectively model device response and to ensure predicted device operation and reliability.

Research on NEMS for high-Q resonator filter array fabrication has recently begun at ARL, in collaboration with research groups at the University of Maryland. While PZT is an attractive material for piezoelectric filters (due to its high piezoelectric coupling coefficient [14]), the operating frequency of PZT resonators is limited to the MHz range, due to the large acoustic time constant of the material. For this reason, piezoelectric materials such as aluminum nitride (AlN), zinc oxide (ZnO), and related compounds are being investigated. The fast acoustic response times of these wide bandgap semiconductor materials translate to theoretical maximum frequencies of more than 100 GHz [15]. Additionally, AlN and ZnO may be grown as thin films (100 nm thick or less) by a variety of techniques, on either silicon substrates (for cost advantages) or a wide bandgap substrate such as silicon carbide (SiC). AlN in particular is chemically inert, radiation hard, and can withstand high temperatures, and chemically harsh environments, making it an excellent candidate for integration of NEMS resonator filters into SiC integrated circuits.

Figure 5. Scanning Electron Microscopy (SEM) Images of Patterns Written at ARL using Electron-Beam Direct-Write Lithography: a) 50nm Quantum Dot Patterns on 100 nm Centers, and b) Nanoscale Gold Finger Structure, with Metal Deposited using a Liftoff Technique after Lithographic Patterning



Detailed device models are required to ultimately enhance filter performance and sensor output quality. The investigation of nonlinear behavior and nanoscale surface effects is planned using ARL's characterization capabilities described elsewhere in this article. In addition, the formation of thin film microstructure is being investigated in collaboration with the California Institute of Technology (Caltech.) Predictive theory, validated by targeted experiments, is being developed to guide materials development, materials selection, and device design. In particular, the piezoelectric materials used as the active components of the NEMS resonator devices are typically composed of domains due either to the deposition technique or to the requirement of unmatched materials systems in the device design. The effects of domain structure in the thin films, where the film thickness may be less than or of the same approximate scale of the domains themselves, is considerably different from that of bulk polycrystalline or textured materials. The resultant device properties may be strongly influenced by the ability to manipulate the domain structure. In the ideal case, a resonator beam formed on a single grain would be expected to exhibit single crystal properties that would result in maximum Q for the device.

The fabrication of MEMS and NEMS devices is performed in ARL's new state-of-the-art 10,000 square foot class 100 Cleanroom. An expansion of this facility is currently being planned to include additional Class 100 and Class 10 fabrication areas. A complement of pattern transfer techniques are available for MEMS/NEMS device fabrication, as listed in

Table 1. Electron beam direct-write lithography is used to generate device features on the scale of tens of nanometers. Figure 5 illustrates 50 nm scale quantum dot patterns with 100 nm spacing exposed in polymethylmethacrylate (PMMA) electron beam resist, and gold finger structures with widths of less than 40 nm, which have been patterned in ARL's fabrication facility. Similar metal patterns are used as masking layers for subsequent reactive ion etching or ion milling techniques, which enable pattern transfer into thin films that form the active device structure. Both anisotropic and isotropic dry etching techniques are employed in the fabrication of free-standing MEMS/NEMS resonators. In addition to developing prototype devices, test structures are specially fabricated to investigate the physical properties of thin film materials. These structures provide feedback to the fundamental materials investigations on grain formation and also facilitate direct measurement of physical properties such as tensile strength

of thin films formed under varying deposition or growth conditions. Such fundamental information will subsequently be used to allow more accurate and sophisticated modeling of devices, enabling the improvements in device operation and design through investigation of materials and device properties at the nanoscale.

Force Detected Magnetic Resonance of GaAs

Force detected magnetic resonance is a recent technique for the detection of magnetic resonance, where the signal is detected mechanically instead of electrically. Magnetic Resonance Imaging (MRI) is the most recognizable nuclear magnetic resonance (NMR) application, as its primary use is for medical purposes. Conventional MRI employs electrical detection, effectively for most objects greater than 10 mm in size. Electrically detecting NMR is very insensitive at smaller scales while mechanical detection on the other hand, is much more sensitive at the nano and low-micron scales. The first proposal and demonstration of a technique for mechanically detecting magnetic resonance was done by A. Gozzini in 1963 [16]. At the time the approach was not practical but research continued. In 1991, John Sidles [17, 18] suggested attaching a small magnetic particle to a cantilever and using the magnetic field gradient from the particle to perform nanometer imaging. Sidles called his approach magnetic resonance force microscopy (MRFM).

MRFM entails measuring the force between the magnetic moment of nuclei (or electrons) in a sample and the magnetic

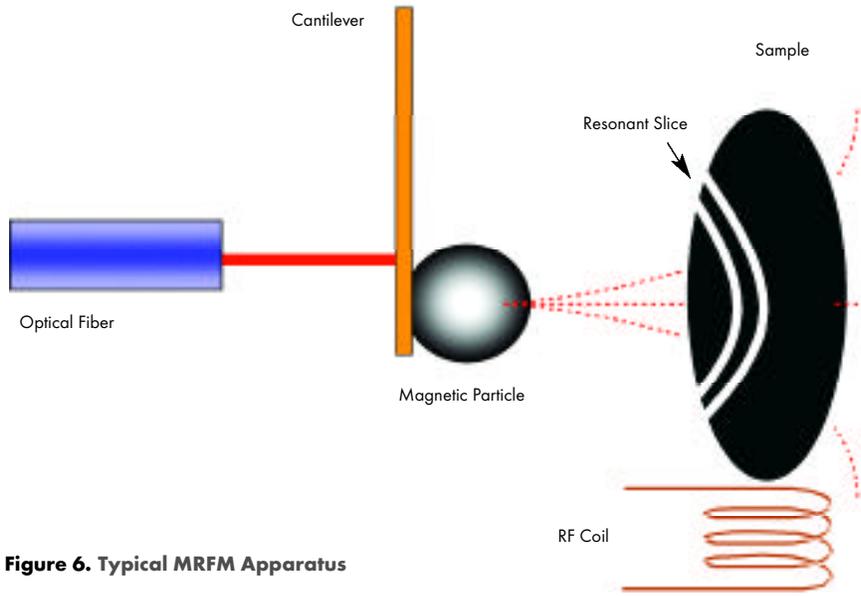


Figure 6. Typical MRFM Apparatus

moment of a nearby magnetic particle (Figure 6). A magnetic particle is attached to a microcantilever, and the sample is placed nearby. The sample contains nuclei that have an associated magnetic moment. The magnet mounted on the cantilever feels a force from the sample, thus displacing the cantilever. The two magnets either attract or repel each other depending on their relative orientation.

By using a combination of amplitude and frequency-modulated RF radiation the sample magnetic moments are cyclically 'flipped'. Cyclical flipping of the magnetic moments, or magnetic resonance, occurs when the energy of an individual RF photon (energy = Planck constant times frequency, or $E=hf$) equals the energy difference between the nuclei's energy levels. Each nuclei has energy levels that are due to the relative orientation of its magnetic moment with respect to a background magnetic field (parallel or antiparallel). For example, magnetic resonance for ^{75}As (Arsenic-75 isotope) at 1 T (Tesla) occurs at a frequency of 7.2919 MHz and is 51.56 MHz at 7.07 T. The difference between the energy levels is a linear function of the

magnetic field strength. When the RF is in resonance with the energy difference, the nuclei either absorb energy or are stimulated to emit energy, thereby oscillating between the two energy levels. The nuclei's oscillation between energy levels oscillates the nuclei's magnetic moment between parallel and antiparallel to the magnetic field.

As the two magnets cyclically attract and repel each other, the cantilever will begin to oscillate. This oscillation is detected by a fiber-based interferometer. If Q is the mechanical quality factor of the cantilever, applying an oscillating force at the

mechanical resonance frequency of the cantilever results in a Q enhancement of the cantilever's amplitude. Thus, the signal is mechanically amplified at least 10,000 times, making detection with the fiber interferometer easier.

A number of groups have reported force-detected NMR in solids. Rugar was the first to report an NMR signal using MRFM techniques [19], exhibiting an orders-of-magnitude improvement over conventional NMR. The magnetic particle creates a changing magnetic field across the sample that assures that only nuclei within a narrow slice experience the correct value of magnetic field to be in resonance with the RF. Nuclei outside of the *resonant slice* are at the wrong magnetic field to be in resonance with the RF. The slice-selective character of MRFM allows a 3-D image of the sample to be obtained by scanning the magnetic particle with respect to the sample in 3-D [20].

The proximate goal of our research is force detection and imaging of nuclear magnetization in as-grown material and in as-fabricated Group III-V (of the periodic table) semiconduc-

Table 1. Partial List of Capabilities for MEMS/NEMS Device Processing in ARL's Class 100 Cleanroom Facility

E-beam lithography	Dielectric (oxide/nitride) dry etching	Wafer-to-wafer alignment
Contact lithography	Ion milling	Anodic and fusion wafer bonding
Photolithography cluster tool	PZT reactive ion etching	Variable angle spectroscopic ellipsometry
UV photostabilization	Laser Doppler vibrometry	Wafer bow stress measurement
Downstream plasma ashing	Metal sputtering	Nanospec film thickness analysis
Mask making	Metal/compound e-beam evaporation	Four point probe analysis
Silicon deep reactive ion etching (DRIE)	Plasma Enhanced Chemical Vapor Deposition (PECVD) oxide/nitride	Profilometry
Isotropic silicon etching	Low Pressure CVD oxide/nitride	
Deep dielectric etching	Sol-gel PZT	
Refractory metal etching	Wet and dry thermal oxidation	

tor devices. As a step toward this goal, we have constructed an MRFM apparatus suitable for force detecting NMR at 4 K. We applied the technique to observe ^{69}Ga , ^{71}Ga , and ^{75}As in GaAs, increasing the number of isotopes observed with force detection from four (^1H , ^{19}F , ^{59}Co , and ^{23}Na) to seven [21]. The sample we examined was a 3- μm epilayer of GaAs, doped at $0.6 \times 10^{18} \text{ cm}^{-3}$ Si and $2.0 \times 10^{18} \text{ cm}^{-3}$ Be. A hand-cleaved rectangle of this material ($\sim 210 \mu\text{m} \times \sim 150 \mu\text{m}$) was then attached to the cantilever ($k \sim 0.05 \text{ N/m}$) using silver-filled epoxy. This cantilever was coated with 0.2 μm of Au on each side to enhance thermal conductivity, and when loaded it had a resonance frequency of 1.034 KHz, and $Q = 154$ at 5 K in the presence of He exchange gas. Q is the quality factor of the cantilever resonance. The magnetic gradient source was a 250 μm diameter Fe cylinder positioned $\sim 35 \mu\text{m}$ from the sample. Because of Newton's third law of motion – for every force there is an equal and opposite force – it does not matter if the sample or magnetic particle is attached to the cantilever. A 1 1/2 turn, 710- μm diameter coil generates the 4-gauss RF magnetic field. The motion of the cantilever was detected by a wavelength-tuned fiber optic interferometer.

Figure 7 displays a force-detected NMR spectrum of our sample observed by sweeping the applied magnetic field at a fixed RF center frequency of 51.56 MHz. All three isotopes are clearly resolved, with cantilever displacements of ~ 1.3 picometers. The large width of the NMR peaks represents the spatial extent of the sample.

As shown, Army researchers have applied force-detected NMR techniques to GaAs and imaged its nuclear isotopes with 1- μm resolution. MRFM technology promises countless applications to material science, medicine, biology, and device fabri-

cation. The ultimate goal for the MRFM community is 3-D imaging of proteins, where the location of every proton in the protein is measured with 0.1-nm accuracy (protein structure). For Group III-V device work, ARL expects to be able to measure such properties as the local value of the electric field; the shape of electron wavefunctions in quantum wells; and 3D strain, internally and nondestructively in as-grown material and as-fabricated devices.

Conclusion

The potential of nanostructures seems limitless in providing detailed information on the cellular, molecular and even atomic level processes. Substantial advantages have already been realized in radiation detection as well as electronic displays. Revolutionary detection modalities, such as real-time biological threat detection, are on the horizon. The future undoubtedly will bring more exciting developments which will advance the state-of-the-art and in the process, provide our military services an additional edge over our adversaries.

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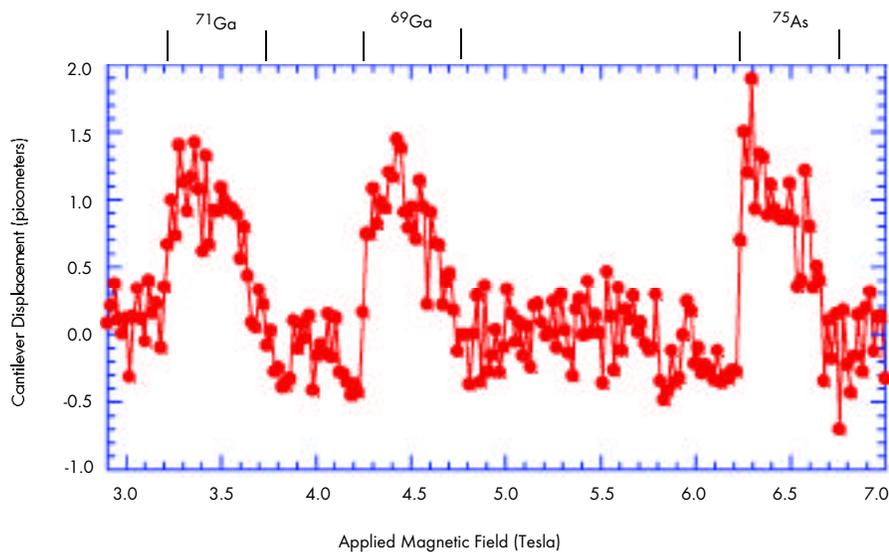


Figure 7. Typical Plot Output for an MRFM

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Fabricating the Next Generation of Electronics from Molecular Structures

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DARPA

Introduction

Miniaturization of electronics brings a multitude of benefits, particularly when a number of disparate functions are integrated onto the same substrate. In the case of the ubiquitous microprocessor chip, the substrate itself is the chip. Its functions are logic, memory, and control circuitry, which deal with the information flow both on and off the chip. Tremendous gains in reliability were obtained by integrating these functions within the same device. These initial gains were mostly due to eliminating connections between individual chips of first generation integrated circuits, as well as reducing the total number of parts. Since that time, miniaturization has driven up the number of individual transistors on chips to well over 10 million. It has also resulted in a multibillion dollar industry which represents a significant fraction of the US Gross Domestic Product. Integrated chips are now in most modern conveniences, such as alarm clocks, coffee makers, and most forms of public and private transportation.

The microelectronics industry is driven by two purposes: the development of new applications and the miniaturization of existing ones. This is why most consumers find buying a new computer every few years irresistible, realizing upwards of a six-fold increase in the performance for the same number of dollars they spent three years before. The process of miniaturization is characterized by 'Moore's law', named after Gordon Moore, the founder of Intel, who first noticed that the number of transistors on a chip doubled every eighteen months. However, this is not a law of physics, but rather a law of economic survival. Companies that can't keep up with this frenetic pace soon find they are uncompetitive, and then fail. Compounding this challenge is the fact that as the integration level increases, the cost of manufacture per unit area of chip must remain the same.

A version of Moore's law is represented in Figure 1, plotting the characteristic dimension of manufactured integrated circuits (ICs) over the last forty years. Many predicted 'ends' to Moore's law have come and gone. For example, at one time it was thought impossible to manufacture a chip with feature sizes much below a micron. New approaches are actively being developed to allow manufacture of chip features down to 20 nm (2/100 of a micron) in size.

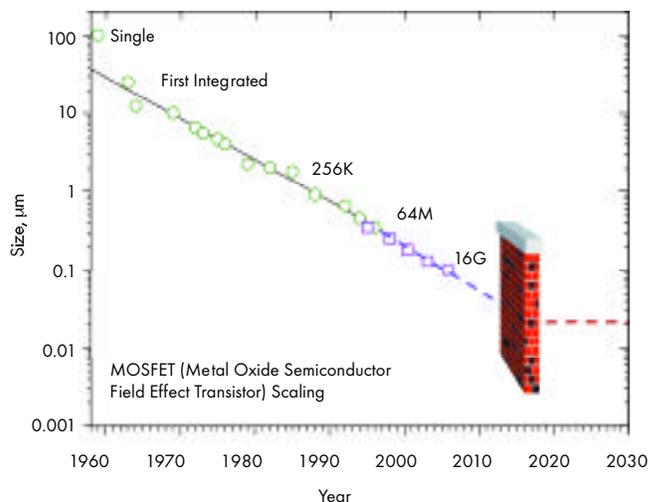
Now we are faced with the end of Moore's law being determined by the physics of the transistors and circuits themselves, presently projected to be around 20-30 nm. Below this size, it becomes increasingly difficult (i.e. expensive) to get these small

transistors to turn off, leading to unacceptable power dissipation. While this problem may be solved by innovative devices and circuit design, the transistor size is rapidly approaching the point when there are so few atoms in the critical regions of the transistor that the underlying solid state (i.e. bulk material) physics begins to break down.

So is there a different paradigm for the manufacture and integration of switches and memory elements? Given that we are looking for devices that have dimensions around 10 nm and lower, it is natural to turn to the chemist who after all is extremely skilled at working in this size regime. The question then becomes, can we design individual molecules that have a specific electronic functionality? Anticipating success, two further questions come to mind. First, can we look for additional help in assembling these molecular components into a useful circuit? Wiring up our molecular memory element to our molecular switch by direct manipulation looks hopelessly impractical apart from heroic onesies and twosies demonstrations. Second, what kind of circuits should we aim for, or more specifically what will the architecture of our memory and logic blocks look like?

These issues also represent the three thrusts of the DARPA Molecular Electronics program and the remainder of this

Figure 1. Recent IC Developments Have Followed Moore's Law



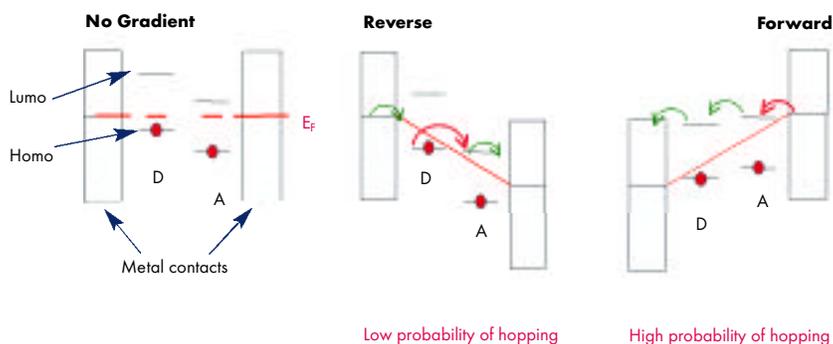


Figure 2. A Schematic of a Molecular Rectifier

article is framed accordingly. The last section will briefly discuss the prospects for molecular electronics and where we might see these first commercial products emerge.

Devices

To date, chemists' ingenuity in designing and synthesizing electronically advantageous molecules has rather outpaced engineers' ability to reliably test their properties at the single molecule level. However, this trend has begun to change as a number of ways of studying electronic transport of single (or small numbers of) molecules have been reported. As a result, the pace of molecular design optimization is accelerating.

One of the landmark papers on conduction through single molecules was published by Aviram and Ratner [1]. They pointed out that if one could couple a readily oxidizing group (D) to a readily reducing group (A), the alignment of the lowest unoccupied molecular orbital (LUMO) and highest occu-

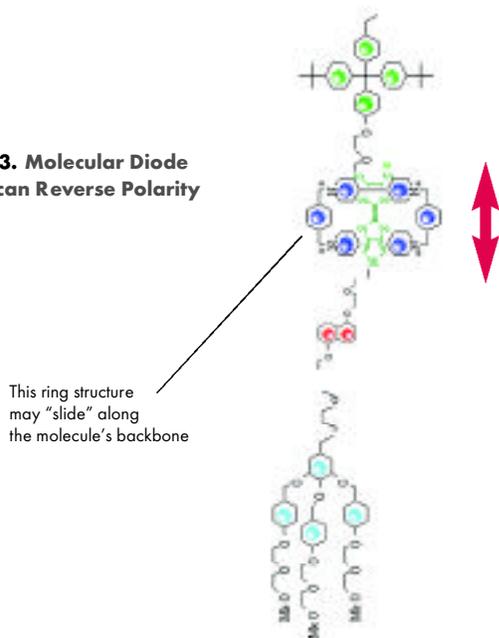
pled molecular orbital (HOMO) would be such that electron hopping (the main mode of electronic conduction in single molecules) would be easier in one direction than the other (Figure 2). This would result in a molecular diode. While straight forward in principle, this has been difficult to demonstrate. Not so much because of the difficulty in synthesizing the molecules, but because of the difficulty in testing them.

An example from the work of Jim Heath and Fraser Stoddard at UCLA [2] is somewhat more complicated and

a full mechanistic study continues. The molecule, an example of which is shown in Figure 3, is a member of the rotaxane family. The groups at either end of the molecule are designed to bond to the electrode surfaces. The area of interest is the center of the molecule, which is comprised of two electron-donating (oxidizing) groups connected by a short spacer. They are surrounded by a ring which has a positive charge. This ring can move up and down the backbone of the molecule and has a sufficiently positive charge to change a donor group to a net acceptor (reducing group). This motion can be induced by oxidizing/reducing the molecule. The net result is an I/V characteristic akin to a diode which reverses polarity! The oxidation/reduction is caused by raising the voltage across the ends of the molecule above a threshold (of a few volts). This is a particularly fascinating characteristic, as there is no equivalent two-terminal device in the solid-state world. The applications to memory are obvious, but Heath and his collaborators in Stan Williams' group at Hewlett-Packard (HP) Labs are also looking at logic applications and are continuing to refine the molecular design.

A second example, which works on a slightly different principle, comes from the collaboration of Jim Tour (a chemist at Rice University) and Mark Reed (an engineer at Yale University) [3]. The I/V characteristics, presented in Figure 4, show a negative differential resistance (NDR) and is reminiscent of a resonant tunneling diode, although it is believed to be governed by a different mechanism. For example, it has been proposed that the discontinuities in the characteristic are due to successive oxidations of the molecule (included on the I/V characteristic). This changes the conductivity of the molecule dramatically as each extra electron is taken on. The inset shows the electron orbital calculations of Jorge Seminario at the University of South Carolina [4]. He has correlated the oxidation states with an overlap of the electron orbitals which favor conduction in the "on" states of the molecule. In the "off" state, there is no such pronounced overlap. Interestingly, his results suggest a conformational change (a twisting of the central ringed group) associated with this conductivity change. Some experimental findings supporting the importance of this conformational change were recently published by Paul Weiss's group at Pennsylvania State University [5]. They measured the switching rates of Tour-Reed NDR molecules through careful Scanning

Figure 3. Molecular Diode which can Reverse Polarity



Tunnelling Microscopy (STM) measurements of individual molecules in a background of an inert alkane SAM (self-assembling molecule). One of Weiss' main conclusions was that the local order (i.e. packing) was extremely important and that NDR molecules could effectively be locked into one of its conduction states if it were not given "room to move" [6].

While progress in single molecular devices has been impressive, they have yet to be optimized. Molecular devices developed to date have limited operating windows. For example, the results reported above were tested and evaluated at a temperature of 60K. However, this class of molecules is currently being re-engineered to work at higher temperatures. Another issue key to the performance of molecular devices is that of the end groups (often referred to as alligator clips) which bind the molecules to electrode metals. In fact, it turns out that the current that can flow through an individual molecule is often dominated by conduction through/across the alligator clips. To date, thiol end groups have been mostly used as their chemistry is reasonably well understood and they form stable, covalent bonds with a gold surface. However, they by no means provide the best 'ohmic' contacts.

Assembly

Now that chemists are enjoying a degree of success in designing molecules with electronic functionality, the key challenge turns to the assembly of these components into viable circuits. One problem is that the molecules are so small (nanometer scale) that none of our existing tools can manipulate them at anything remotely close to a viable rate. Some interesting results have been published using proximal probes to manipulate atoms and molecules. But even the most ardent devotees of this work admit that it is far too slow for fabricating circuits of any complexity or number. Similarly, even the most advanced lithographic tools cannot match the resolution of molecular devices. Instead, we must look to other ways to put molecular circuits together. One approach would be simply to 'synthesize' the entire circuit as a single (very large) molecule. At the present time, this is not a feasible concept, although we will probably see the synthesis of increasingly large functional molecules in the years to come.

Carbon nanotubes provide a possible framework for building such large molecules. To date, some novel devices have been reported using the nanotubes as the conduction channel for miniaturized transistors [7]. Charlie Lieber at Harvard University has also used crossed nanotubes to produce devices with very small active areas ($<10 \text{ nm}^2$) [8]. However, the actual device sizes are dominated by the contacts to the nanotubes

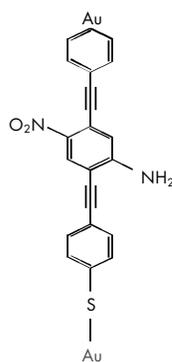
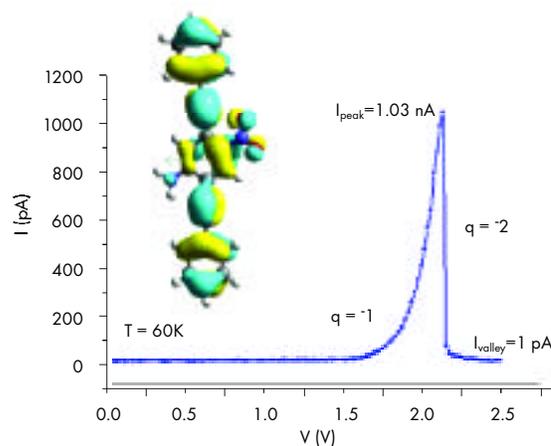


Figure 4. Nitroamine Molecule and Its Behavior



being many orders of magnitude larger than the active areas. One reason for this is the difficulty in manipulating nanotubes. To fully exploit the scaling possible with this device configuration, the nanotubes must be positioned with nanometer precision. While impressive advances in directed nanotube growth and fluidic manipulation have been made, we are still some way from being able to fully exploit the benefits of these nanoscale components.

We again look to the chemist for additional help in putting circuits together from molecular devices. Ordered films can be formed from disordered solutions of monomers, designed so that one end has an affinity for a particular substrate material. When this affinity results in a covalent bond (as in the case of a monomer with a thiol end group and a gold substrate), the process is described as self-assembly. Langmuir-Blodgett films are similar, but the monomer-substrate bond is weaker. In both cases, the monomers are designed such that the densely packed film on the substrate is a lower energy configuration than the disordered solution. Here, the energy is related to the bond formed between monomer and substrate. But there are other possible energy drivers such as surface energy, electrical energy, etc.

The challenge then becomes to design a configuration where the minimum energy state corresponds to something resembling a functional circuit. While something of the complexity of a conventional microprocessor would appear to be out of reach, simpler building block circuits such as a memory block or logic gate(s) could be put together in this way. Even so, it appears a series of assembly processes will be needed operating at successively larger length scales. At this point, the research is not as advanced as with molecular devices. Nonetheless, some first steps have been taken.

Under DARPA sponsorship, the Penn State Group headed by Theresa Mayer and Tom Mallouk has demonstrated at least two levels of hierarchical assembly. They have been working with metallic nanowires fabricated by a process of templated electroplating. Porous membranes can be obtained with a large

number of essentially identical diameter tracks. This provides the template for the plating. Functionality can be built into the nanowires. For example, some of the functional molecules described above can be included by interrupting the plating and self-assembling the molecules in the middle of the metallic nanowire. The plating can then be continued. The resulting functional nanowire can be manipulated in a number of ways. One way is to use DNA as a 'glue' to adhere the nanowires selectively to a substrate (or to each other). The Penn State team has also designed a novel circuit where the metallic nanowires will 'assemble' between two landing pads, driven by a minimization of the electrical (capacitive) energy of the system [9]. Furthermore once one nanowire has bridged the gap, the process self-limits so one, and only one, nanowire will be positioned across the landing pads. The group is continuing to refine these assembly methods and is also looking at other techniques operating at larger length scales.

So a series of hierarchical assembly steps seem possible and are beginning to forge a path which could fabricate a circuit with a degree of complexity and computational functionality per unit area greater than extensions of Si-based microelectronics. However, these assembly processes are energy driven, so it seems inevitable that there will be defects such as incorrectly positioned structures and/or molecules. Thus to be useful, the circuit architecture must be tolerant of a significant defect level.

Architecture

Molecular memory based on molecular devices (of the type described in Section 2) appears feasible. However, to fully exploit the miniaturization benefits of molecular electronics, defect-tolerant circuits are needed. In contrast, today's volume-produced microelectronic chips are extraordinarily intolerant of defects. All of the tens of millions of transistors in a microprocessor must be functional, or the chip is no more useful than the pile of sand from which the silicon was made. An example of a functional computation machine containing defective components is the HP Teramac [10]. The key to the Teramac's operation is the inclusion of significant redundancy of components and interconnections. Further, a period of 'self evaluation' is necessary to identify and route around the defective components. In other words, the machine was first put together and then examined to find out what was functioning usefully.

More recently, these ideas have been extended to the circuit level. The same group at HP that developed the Teramac recently patented a design for a multiplexer, where the connections between the address lines and the data lines are random. In a normal multiplexer, N data wires are addressed by $\log N$

address lines, that is, each address line can be thought of as representing a power of 2 in the address of the data line. The group pointed out that by providing extra address lines, there is a vanishingly small probability that all the N data lines will *not* be addressable even if the connections between the address and data lines are random [11]. As the required number of address lines scales with the logarithm of the number of data lines, for a large array, the added area taken by the extra address lines is insignificant. A discovery phase is needed for such a circuit as there will be address duplication (some data lines will not have unique addresses). Thus, by providing redundancy and allowing for the discovery phase, it is hoped to fabricate a functioning circuit with a non-deterministic (random) critical patterning step. Many believe that fabrication of this type of random structure may be amenable to chemical-based assembly.

Other researchers are pursuing similar techniques to assemble circuits with a degree of randomness that can, nonetheless, perform a useful information processing function. The key issue becomes the time required for the discovery phase along with any modifications that must be made to the structure of the circuit. These ideas are completely contrary to present day functional circuit design. Molecular electronics offers the potential of miniaturization and reduced manufacturing cost, with the caveat that circuit architecture will not be completely understood at the outset. This is the most radical part of current molecular electronics research.

Summary: What's Next

For a disruptive technology such as molecular electronics to move from the research lab to commercial products, an overwhelming economic-based case needs to be made. At present, the microelectronics industry can look forward to at least a decade of continued prosperity based on miniaturization. Thus, early introduction of molecular-based technology will probably be in a niche product that marries the advantages of molecular electronics with the existing Si-dominated infrastructure. An example might be non-volatile (or limited volatility) memory for digital cameras and other storage-intensive applications. These applications require dense memories with volatilities measured in weeks, which can be manufactured efficiently and economically.

The field is moving rapidly and there is considerable optimism as to what will be possible in the not too distant future [12]. Whether this optimism can be turned into a viable technology remains to be seen. Now that there have been convincing demonstrations of molecular devices with useful electronic functionality, the key challenges will be the assembly of these molecular components into functional circuits.

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Christie has authored over 105 technical publications and holds 13 patents. He is a Fellow of the American Vacuum Society (AVS) and also a Senior Member of the IEEE. He has served as Secretary of the Nanometer Science and Technology Division of the AVS since its inception in 1992 and was elected to the AVS Board of Directors in 1997. Christie was vice chair of the 38th AVS National Symposium in 1991 and chair of the International Program Committee of NANO 3 which was held in conjunction with the AVS National Symposium in 1994. In 1996, he edited a special issue of the Proceedings of the IEEE on Nanometer-scale Science and Technology. He was the Program Chair in 1998 of the 42nd International Conference on Electron, Ion and Photon Beam Technology and Nanofabrication. In 2000, he was co-chair of NANO 6 and chair of the Gordon Research Conference on Nanostructure Fabrication.

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Engineering the Future of Nanophotonics

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Just as electronic devices continue to shrink in size and provide greater computing power and storage, photonic devices will follow the same trend, providing greater efficiency and functionality. However, increasingly smaller photon emitters, detectors, waveguides, filters, and other optical components face limitations of scale. As the size of these devices approaches the wavelength of light (< 1 micron), it grows increasingly difficult for them to confine photons in the dielectric structure. A promising solution to this photon leakage problem is provided by the concept of photonic band engineering, which allows the control of photon dispersion, transmission, and reflection through the creation of periodic or quasi-periodic dielectric structures.

Photonic Crystals

Photonic crystals (also called photonic bandgap materials) are micro-structured materials in which the dielectric constant (equal to the square of the index of refraction at optical wavelengths) is periodically modulated on a length scale comparable to the desired wavelength of the electromagnetic radiation. Multiple interference between optical waves scattered from each unit cell results in a range of frequencies that do not propagate in the structure. At these frequencies, the light is strongly reflected from the surface, while at other frequencies light is transmitted.

For example, highly reflective surfaces are routinely constructed from simple layered dielectric structures with alternating layers of high and low refractive indices. One-dimensional

Figure 2. Three-Dimensional Photonic Crystal [2]



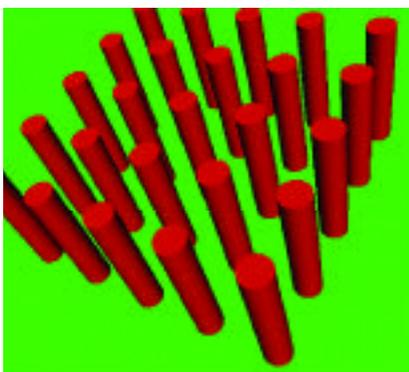
photonic crystals have long been used as anti-reflection coatings or as wavelength-selective mirrors which do not reflect heat, (such as the ones used in dentists' work lights). In two dimensions, one can construct a periodic variation in index of refraction by assembling an array of cylinders, such as the array shown in Figure 1a. A two-dimensional photonic crystal may be either a lattice of air columns in a dielectric material or a lattice of dielectric columns in air. Measuring transmission through the cylinders shows a broad band where the transmission drops to zero (Figure 1b).

A band gap that prohibits propagation in any direction can be created by fabricating a structure that has the proper three-dimensional periodicity in the index, as seen in Figure 2. This bandgap in photon energies is analogous to electron bandgaps in semiconductors. The gemstone opal is a naturally-occurring, three-dimensional photonic crystal. The distinctive color of opal is due to reflected light, the reflection being caused by the partial photonic band gap of the crystal. Therefore, two- and three-dimensional photonic crystals act as novel two- and three-dimensional mirrors. Defects may be created inside photonic crystals by removing or adding dielectric material, thereby

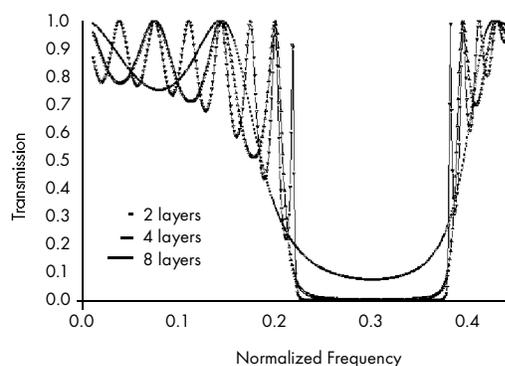
allowing the light propagation to be modified. Photonic crystals with and without defects have been demonstrated at microwave frequencies, but fabricating similar, visible-wavelength photonic crystals would require state-of-the-art nanofabrication techniques.

Waveguides

Photonic crystals are interesting for optoelectronic devices because they make possible the control and confinement of photons in small volumes (on the scale of one wavelength cubed). The use of defects in photonic structures has the



(a)



(b)

Figure 1. Two-Dimensional Photonic Crystal and Its Calculated Transmissivity [1]

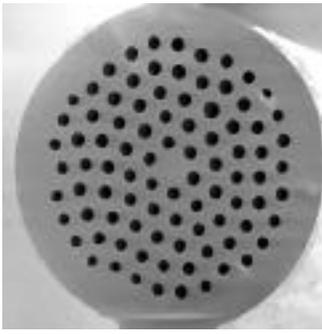


Figure 3a

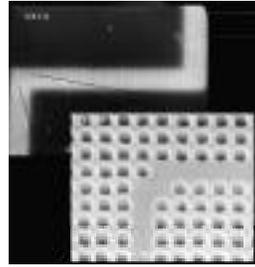


Figure 3b

Figure 3. Photonic Crystal Optical Fiber [3] and Integrated Photonic Waveguide [4]



Figure 4a

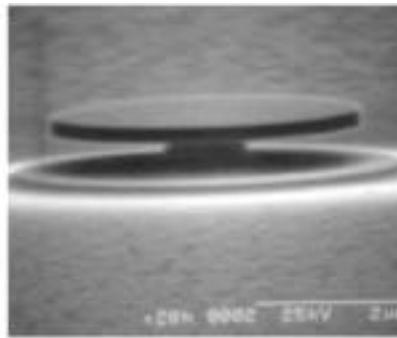


Figure 4b

Figure 4. Vertical Cavity Surface Emitting Laser [5] and Microdisk Laser [6]

potential for guiding light through sharp bends in integrated optical systems. The tighter the bends that can be made, the more compact the integrated photonic system can be. Photonic crystals therefore provide a revolutionary capability to shrink integrated photonic systems dramatically.

On the other hand, photonic crystals can be drawn into optical fibers for low loss, long range communication and routing of information. Two types of photonic crystal fiber have been demonstrated. The first consists of a two-dimensional photonic crystal with a defect in the center (Figure 3a). The photonic crystal is replicated in the third (non-periodic) dimension many meters. Light is guided down the defect and confined by the two-dimensional photonic crystal surrounding it. The second consists of a one-dimensional photonic crystal wrapped into a long cylindrical tube (Figure 3b). Again, light is guided down the center and confined by the highly reflective photonic crystal. In both cases, light is guided down an air core, in contrast with current optical fiber which confines light in a glass core. As a result, low loss light guiding can be accomplished at any wavelength, not just the wavelengths of lowest absorption in glass fiber (1.3 and 1.55 microns). Reduced optical nonlinearities promise much larger transmission bandwidths than are currently achievable, and operation at visible

wavelengths promise much higher detection efficiency using state of the art avalanche photodiodes.

Resonators and Lasers

The use of periodic structures to form resonators and lasers is not new. One-dimensional photonic crystals are simply dielectric mirrors, and two such reflectors facing each other form a Fabry-Perot resonator. Vertical cavity surface-emitting lasers (VCSELs) are formed by placing a quantum well active region in the “defect” space between such a Fabry-Perot resonator. Increased lateral confinement of the photons is achieved through total internal

reflection by etching the VCSELs into narrow posts such as shown in Figure 4a.

Using the same principle of total internal reflection, a circular “whispering gallery mode” resonator can also be used as a laser cavity (Figure 4b). Such lasers have greater confinement and higher cavity energy density (Q) than conventional VCSELs, yielding lower lasing thresholds but weaker, omnidirectional emission. Slight deformations of the microdisk have permitted more directional emission.

To gain even more control over the emission and threshold, higher dimension photonic crystal resonators may be used. Two-dimensional photonic crystals with defects have been fabricated in Si, GaAs and InGaAsP materials to couple filters and switches with low loss. Point defects can be used to form laser cavities, such as a missing hole in a hexagonal array of holes, as depicted in Figure 5. Micro-cavities with a mode volume of 0.03 cubic microns have been fabricated in InGaAsP and lasing was observed at a wavelength of 1.5 microns with optical pumping.

These defects could potentially increase the spontaneous emission rate of photons in the visible or near-infrared region. Larger defects provide higher output powers because of the greater active material volume. The large cavity shown in

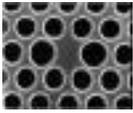


Figure 5a

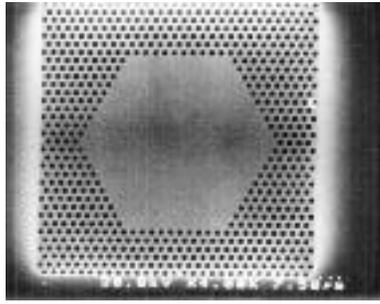


Figure 5b

Figure 5. Single Defect and Large Defect Cavities In 2D Photonic Crystals [7]

Figure 5 has modes similar to the whispering gallery modes of the microdisk laser (Figure 4b).

Quantum Information Science

One of the most exciting potential applications for nanophotonic devices may be the demonstration of the first quantum information processing units. Unlike classical bits of information which must be either in the “0” or “1” state, quantum information is based on the laws of quantum mechanics which permit a “quantum bit” or “Qbit” to be in a superposition of both states simultaneously. Recently, an all-optical scheme for performing quantum computing was proposed using linear optical components and the nonlinear measurement process. A version of this quantum computer may someday be constructed using photonic crystal-based nanophotonic components.

Another goal of quantum information processing is to trans-

port quantum bits and teleport quantum information over optical fiber. To do this, two new nanophotonic devices are needed: single photon sources and low loss optical fiber. Recently, groups at Stanford University and the University of California, Santa Barbara demonstrated the first semiconductor single photon sources based on VCSELs and microdisk resonators, respectively. Likewise, sources of entangled photon pairs and atomic or solid state systems for quantum logic and quantum memory may work more efficiently at wavelengths other than 1.3 or 1.55 microns. Low loss photonic crystal fiber may prove to be ideal means for transporting and preserving these fragile photonic quantum states in the visible wavelength region.

References

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- [6] Courtesy of Atac Imamoglu, University of California, Santa Barbara.
- [7] Courtesy of Axel Scherer, Cal Tech. ■



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