Nanotechnology Research & Development at the Department of Defense

Dr. Clifford Lau
Office of Naval Research
703-696-0431
lauc@onr.navy.mil

Historical Perspective

DoD recognized the importance of nanotechnology in the early 1980s when research sponsored by DoD began to approach nanometer scale, although we didn't call it nanotechnology at the time.

1980	1990	2000
Microelectronics Physics Chemistry Materials Molecular biology	→	Nanotechnology

National Nanotechnology Initiative, 2001

- Initiative was planned and coordinated by interagency working group
- Goal was to double the federal government investment in nanotechnology over that of FY2000
- Participating agencies

	FY2000	FY2001	FY2002 (estim.)	FY2003 (request)	FY2004 (request)
NSF	$97M	$150M	$204M	$221M	$249M
DoD	$70M	$123M	$180M	$243M	$222M
DoE	$58M	$88M	$89M	$133M	$197M
NASA	$4M	$22M	$35M	$33M	$31M
NIH/HHS	$32M	$40M	$59M	$65M	$70M
NIST/DoC	$8M	$33M	$77M	$69M	$62M
EPA		$5M	$6M	$6M	$5M
DHS(TSA)		$2M	$2M	$2M	$2M
USDA		$1.5M	$1M	$1M	$10M
DOJ		$1.4M	$1M	$1M	$1M
Total	**$270M**	**$464M**	**$654M**	**$774M**	**$849M**

Note: Some agencies do not have appropriation yet in FY03.

DoD Investment on Nanotechnology

	FY2000	FY2001	FY2002	FY2003	FY2004 Planned
DoD	**$70M**	**$123M**	**$180M**	**$243M**	**$222M**

OSD	$ 28M
DARPA	$142M
Army	$ 29M
Navy	$ 31M
Air Force	$ 13M

OSD	$ 28M
DARPA	$117M
Army	$ 30M
Navy	$ 29M
Air Force	$ 18M

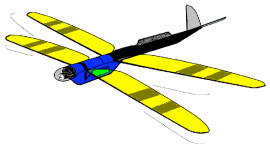
Note: FY04 budget is estimate only, especially with high uncertainty in DARPA.

NNI Science and Technology Areas

- Long-term fundamental nanoscience and engineering research
  - Fundamental understanding of nanometer size building blocks
  - Materials and manufacturing
  - Nanoelectronics
  - Medicine and health care
  - Chemical and pharmaceutical industries
  - Biotechnology and agriculture
  - Computers and information technology
  - National security

- Grand challenges
  - Increase memory storage density by a thousand fold
  - Material manufacturing from atom by atom up
  - Develop materials 10 times stronger than steel
  - Improve computer speed/efficiency/memory by a million fold
  - Cancer cell detection and drug delivery
  - Cleaner environment and potable water
  - doubling the efficiency of solar cells

DoD Focused Areas in NNI



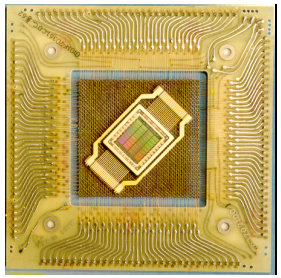
* NANOELECTRONICS/NANOPHOTONICS/NANOMAGNETICS
  Network Centric Warfare
  Information Dominance
  Uninhabited Combat Vehicles
  Automation/Robotics for Reduced Manning
  Effective training through virtual reality
  Digital signal processing and LPI communications

* NANOMATERIALS “BY DESIGN”
  High Performance, Affordable Materials
  Multifunction, Adaptive (Smart) Materials
  Nanoengineered Functional Materials
  Reduced Maintenance costs

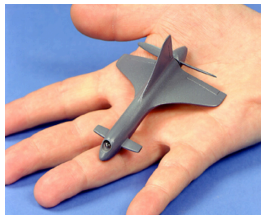
* BIONANOTECHNOLOGY - WARFIGHTER PROTECTION
  Chemical/Biological Agent detection/destruction
  Human Performance/Health Monitor/Prophylaxis

* Both long-term fundamental research and grand challenges

Enhanced warfighting capabilities



* Chem-bio warfare defense
  Sensors with improved detection sensitivity and selectivity, decontamination
* Protective armors for the warrior
  Strong, light-weight bullet-stopping armors
* Reduction in weight of warfighting equipment
  Miniaturization of sensors, computers, comm devices, and power supplies
* High performance platforms and weapons
  Greater stealth, higher strength light-weight materials and structures
* High performance information technology
  Nanoelectronics for computers, memory, and information systems
* Energy and energetic materials
  Energetic nano-particles for fast release explosives and slow release propellants
* Uninhabited vehicles, miniature satellites
  Miniaturization to reduce payload, increased endurance and range



DoD Programs in Nanotechnology

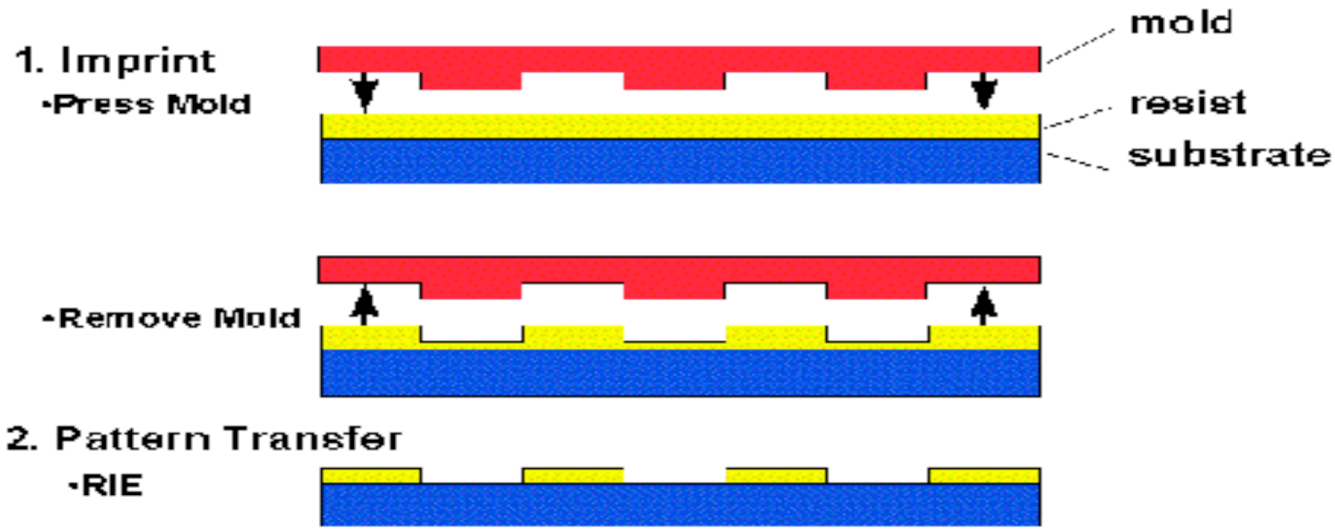
- Army
  Nanostructured polymers, quantum dots for IR sensing, nanoengineered clusters, nano-composites, Institute for Soldier Nanotechnology (ISN)
- Navy
  Nanoelectronics, nanowires and carbon nanotubes, nanostructured materials, ultrafine and thermal barrier nanocoatings, nanobio-materials and processes, nanomagnetics and non-volatile memories, IR transparent nanomaterials
- Air Force
  Nanostructure devices, nanomaterials by design, nano-bio interfaces, polymer nanocomposites, hybrid inorganic/organic nanomaterials, nanosensors for aerospace applications, nano-energetic particles for explosives and propulsion
- DARPA
  Bio-molecular microsystems, metamaterials, molecular electronics, spin electronics, quantum information sciences, nanoscale mechanical arrays
- SBIR
  Nanotechnologies, quantum devices, bio-chem decontaminations
- OSD
  Multidisciplinary University Research Initiative (MURI), DEPSCoR, NDSEG

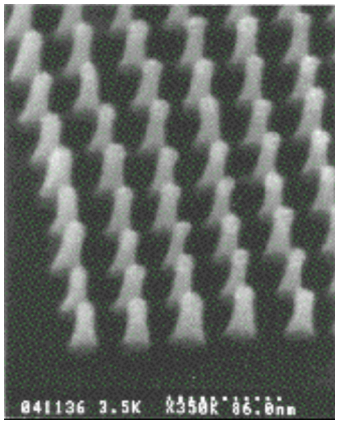
FY01-06 Defense University Research on NanoTechnology

Investigator	Prime Institution	State	DURINT Topic	Agency
Josef Michl	University of Colorado	CO	Nanoscale Machines and Motors	Army
Mehmet Sarikaya	University of Washington	WA	Molecular Control of Nanoelectronic and Nanomagnetic Structure Formation	Army
Michael R. Zachariah	University of Minnesota	MN	Nano-Energetic Systems	Army
Hong-Liang Cui	Stevens Institute of Technology	NJ	Characterization of Nanoscale Elements, Devices, and Systems	Army
Richard Smalley	Rice University	TX	Synthesis, Purification, and Functionalization of Carbon Nanotubes	Navy
Stephen Chou	Princeton University	NJ	Nanoscale Electronics and Architectures	Navy
Randall M. Feenstra	Carnegie Mellon University	PA	Nanoporous Semiconductors - Matrices, Substrated, and Templates	Navy
Subra Suresh	Massachussetts Institute of Technology	MA	Deformation, Fatigue, and Fracture of Interfacial Materials	Navy
Horia Metiu	University of California at Santa Barbara	CA	Nanostructures for Catalysis	Air Force
Mary C. Boyce	Massachussetts Institute of Technology	MA	Polymeric Nanocomposites	Air Force
Paras Prasad	State University of New York at Buffalo	NY	Polymeric Nanophotonics and Nanoelectronics	Air Force
Terry Orlando	Massachussetts Institute of Technology	MA	Quantum Computing with Quantum Devices	Air Force
James Lukens	State University of New York at Stony Brook	NY	Quantum Computing with Quantum Devices	Air Force
Chad A. Mirkin	Northwestern University	IL	Molecular Recognition and Signal Transduction in Bio-Molecular Systems	DARPA/Air Force
Anupam Madhukar	University of Southern California	CA	Synthesis and Modification of Nanostructure Surfaces	DARPA/Air Force
George Whitesides	Harvard University	MA	Magnetic Nanoparticles for Application in Biotechnology	DARPA/Navy

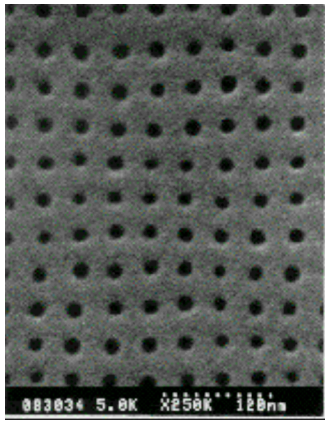
Nanoimprint Lithography

Princeton University, Professor Stephen Chou

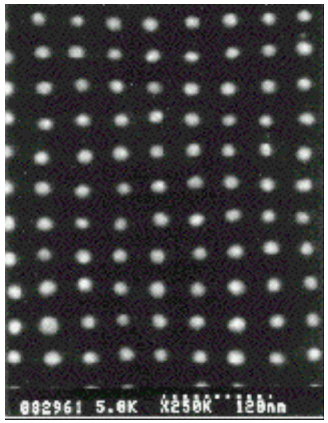




Imprint mold with 10nm diameter pillars



10nm diameter holes imprinted in PMMA



10nm diameter metal dots fabricated by nano-imprint lithography

EVOLVING SUCCESS STORY:
NANOSTRUCTURED COATINGS

1996: First nanostructured coating (WC-Co) produced by thermal spray processing

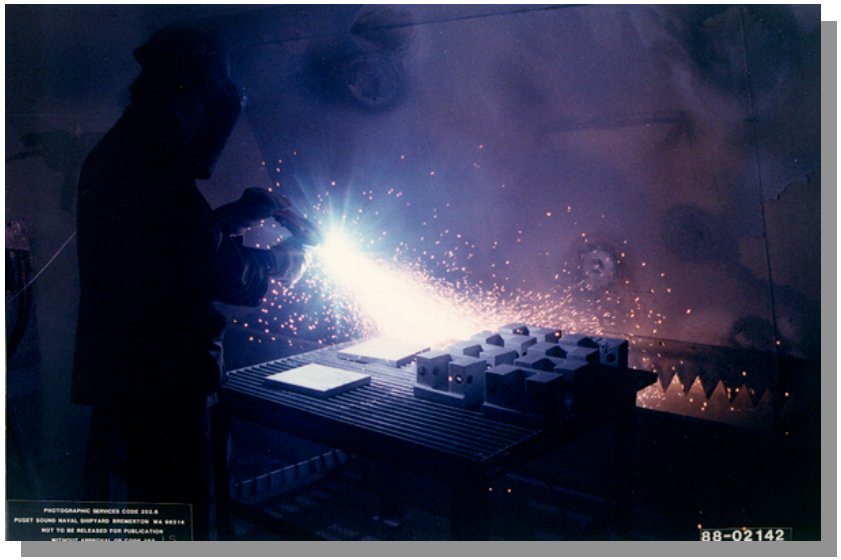
1997: Nanostructured ceramic coatings successfully fabricated using plasma spray

1998: Nanostructured ceramic coatings produced directly from liquid precursors, greatly lowering cost

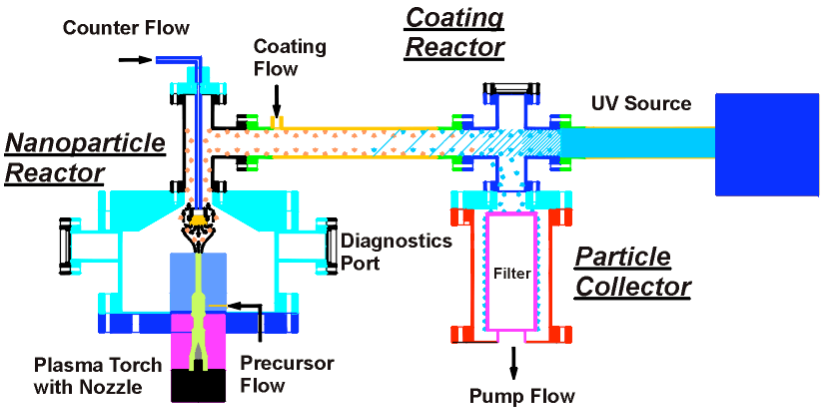
1999: Begin full scale testing of nanostructured coatings on shipboard components.

Kabacoff, ONR

Nanostructured thermal sprayed coatings offer greatly enhanced adhesion, toughness, wear resistance and machinability and thickness (compared to conventional coatings)



Nano-Systems Energetics
University of Minnesota
http://www.me.umn.edu/~mrz/CNER.htm



Nanoparticle Reactor Facility

Objective

Develop new methods for and understanding of the Synthesis, Characterization, and Reactivity of nano-scale energetic materials

Research Areas

Methods for nanoparticle growth and surface passivation.
Sol-Gel methods for generation of nanostructures
Modeling of particle formation from thermal plasmas.
Methods for nanoparticle characterization
Thermochemistry of nanoparticles and nanostructures.
Nanoparticle oxidation kinetics.
Characterize rates of energy release for nanostructures.
Measurement of solid-solid exothermic reactions.
Computational chemistry/physics of nanostructures.

Research Accomplishments

- **Kick-off meeting September 01**
- **Designed continuous flow reactor for nanoparticle production and passivation**
- **Formulated model for nanoparticle formation and growth**
- **Designed experiments for characterization of size, composition and reactivity of nanoparticles**

DURINT 2001: Surface Modification Engineered Assembly of Novel Quantum Dot Architectures for Advanced Applications

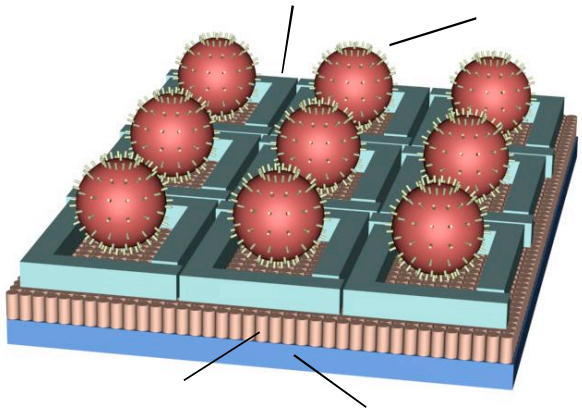
Start Date: May, 01, 2001

University of Southern California; UC Berkeley; Princeton; LSU

OBJECTIVES

• Explore chemical and structural surface modification approaches for realization of regular arrays of integrated semiconductor quantum dots via the use of the self-assembling nature of biochemical macromolecules and stress-driven self-organized epitaxy

• Assess the usage of such nanostructures for quantum devices relevant to applications in data storage, computing, signal processing, and imaging



CHALLENGES

• Developing mutually compatible paradigms and processes for the integrated synthesis of colloidal and epitaxically grown quantum dots

• Examining atomic scale stress/strain distributions and their impact on QD stability and electronic structure

• Developing and understanding approaches to realizing interlaced hierarchical levels of surface structural and chemical patterning on 3 to 100 nm spatial scale

MILESTONES

• Realization of controlled 2D regular arrays of colloidal nanocrystal particles in ultra high vacuum environment of semiconductor epitaxy

• Realization of non-destructive growth of overlayers on above noted 2D arrays

• Realization of high quality electrical and optical response from hybrid integrated colloidal and epitaxically grown quantum dot structures

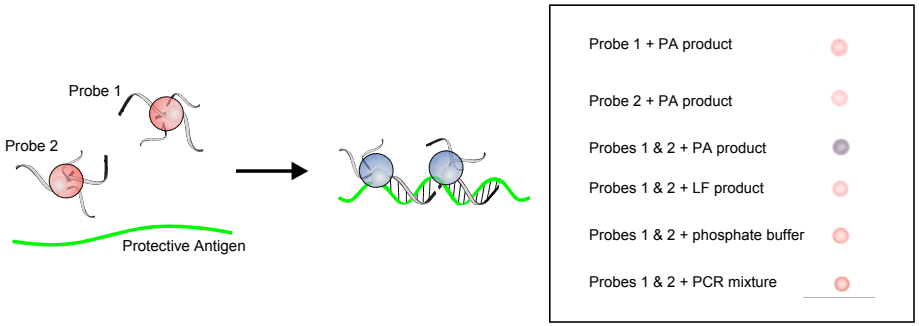
• Demonstration of single or few electron devices (e.g. memory, detector, etc.)

Cluster Engineered Materials

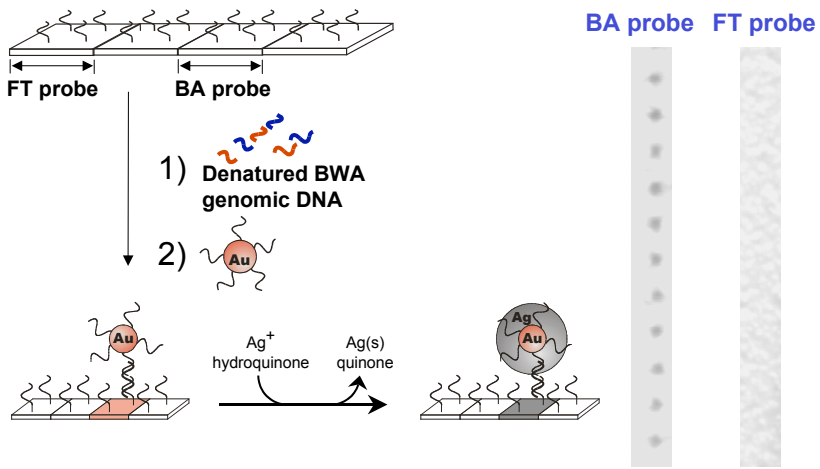
Chad Mirkin, NWU

- Biological agent detection
  - PCR-free bioagent recognition
  - DNA/Nanosphere-based
    - Anthrax detection in solution
      - 30 nucleotide region of a 141-mer PCR product (*blue dot*)
      - Sensitivity: <10 femtomole
      - Detect single BP mismatch
    - Anthrax detection on substrate
      - Agent binds Au cluster
      - Ag: 10^5 amplification
      - Amount: grey scale
  - Tested
    - Dugway PG, 2001
      - 32 parallel tests in 1.5 hrs!
  - Active technology transfer
    - Nanosphere (spin off company)
    - Medical & industrial interest

Colorimetric Detection of Anthrax in Solution



Colorimetric Detection of Anthrax on Substrate

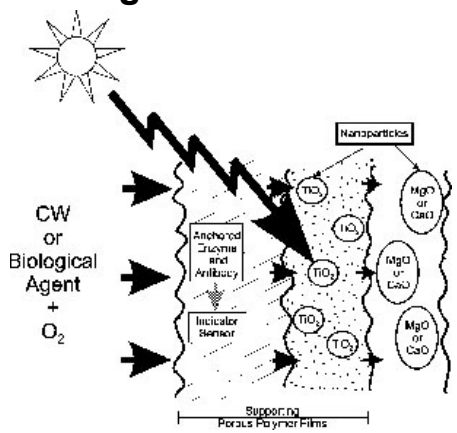


BA = Bacillus Anthracis
FT = Francisella Tularensis

MURI: Photocatalytically Active Nanoscale Scavengers and Sensors for CW and Biological Agents

University of Pittsburgh

GOAL – Develop a multilayer film structure to simultaneously sense and destroy chemical and biological warfare agents .



Schematic Multilayer Scavenger and Sensor Device

DELIVERABLES —

- Polymer-anchored enzyme and antibody scavengers and sensors for CB agents
- Visible-light activated doped-Ti_2O nanoparticles with non-photoreactive porous polymer support catalyzing the destruction of both chemical and biological agents
- Extremely active CaO and MgO and MgO-Cl_2 nanoparticle material for the degradation of CB agents, supported in polymer films

CHALLENGES —

- Integration of both chemical and biological agent sensors and CB catalysts for their destruction into stable multifunctional films or coatings
- Efficient photocatalysis in the visible spectrum
- Integration of the multifunction films into working devices

PRIOR WORK —

- University of Pittsburgh research on Ti_2O photocatalysts and polymer anchored enzymes and sensors
- Kansas State University work on active nanoparticle oxide adsorbents
- Texas A&M University work on antibody-based scavengers

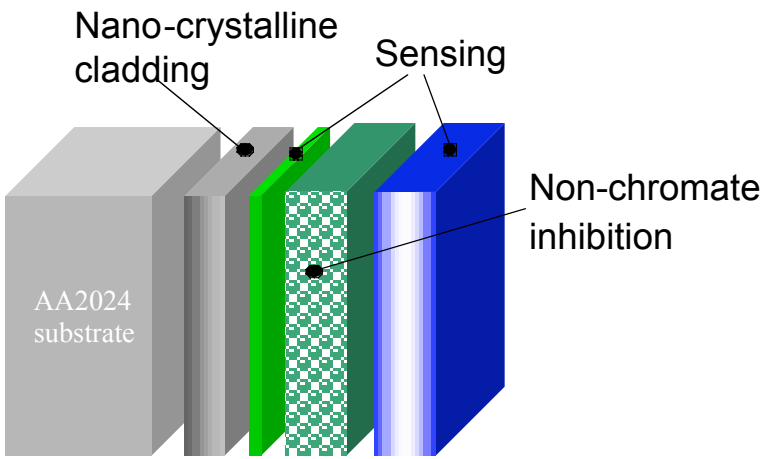
- University of Pittsburgh research on Ti_2O photocatalysts and polymer anchored enzymes and sensors.
- Kansas State University work on active nanoparticle oxide adsorbents.
- Texas A&M University work on antibody- based scavengers.

MURI-01

An Environmentally Compliant, Multi-Functional Coating for Aerospace Using Molecular and Nano-Engineering Methods

University of Virginia

10/15/01



APPROACH

- Multi-coat system built upon thermally spayed amorphous Al-alloy cladding
- Combinatorial chemistry and nano-encapsulation to identify/deliver non-chromate inhibitors
- Colloidal crystalline arrays, and other molecular probes to provide sensing

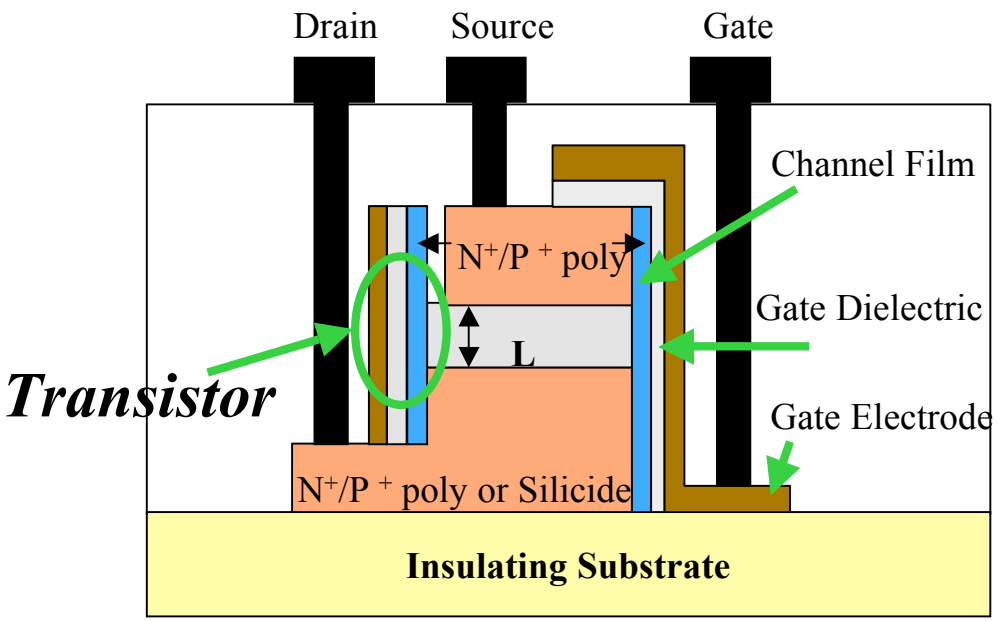
GOALS/OBJECTIVES

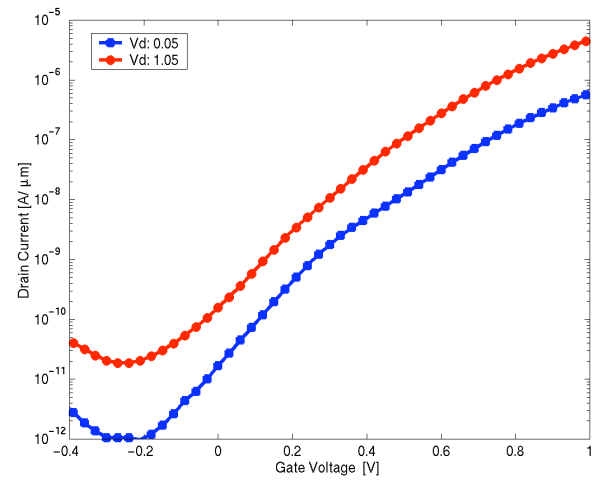
- To develop a new multi-functional coating system for military aircraft
- Coating will sense corrosion and mechanical damage
- Initiate mitigation response to mechanical and chemical damage
- Provide corrosion protection and adhesion using environmentally compliant materials

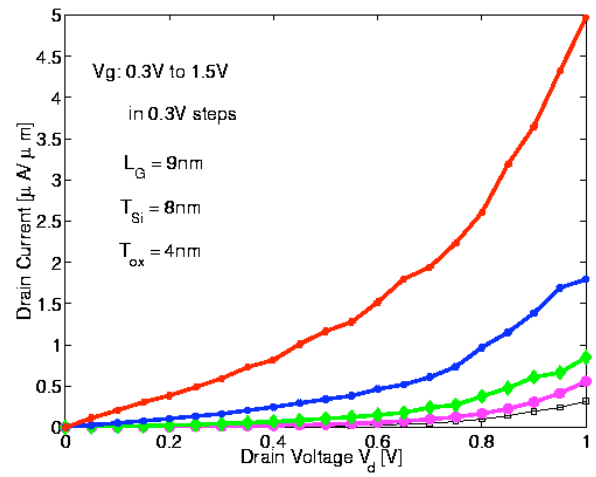
DOD TECH PAYOFF

- Will provide significant advancement in corrosion protection, life cycle costs, and mission safety

9 nm Vertical Field Effect Transistor







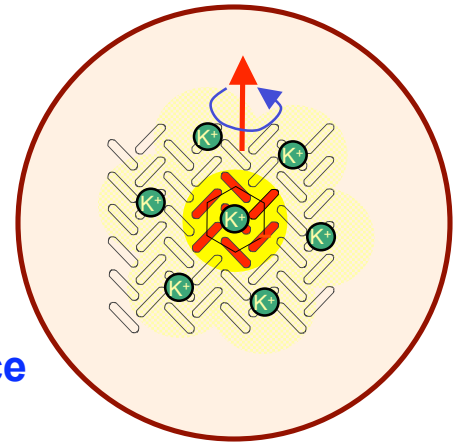
DARPA HGI Program, PI - K. Saraswat (Stanford U.)

D. Allara and B. Hasslacher (Penn State University);
AFOSR Grant: ***Self-Assembled Molecular Spin Arrays for Quantum Computation***

- **Molecular Spin Arrays**: **A novel, robust approach to the physical realization of a quantum computer**

- **Major issue**: **the fabrication and testing of a real quantum computer lags far behind the advances in the the theory of quantum computing because of the need for a viable physical platform**

- **Critical Need**: **Development of an easily fabricated, organized array of spins with readily controlled lattice parameters and spin types**

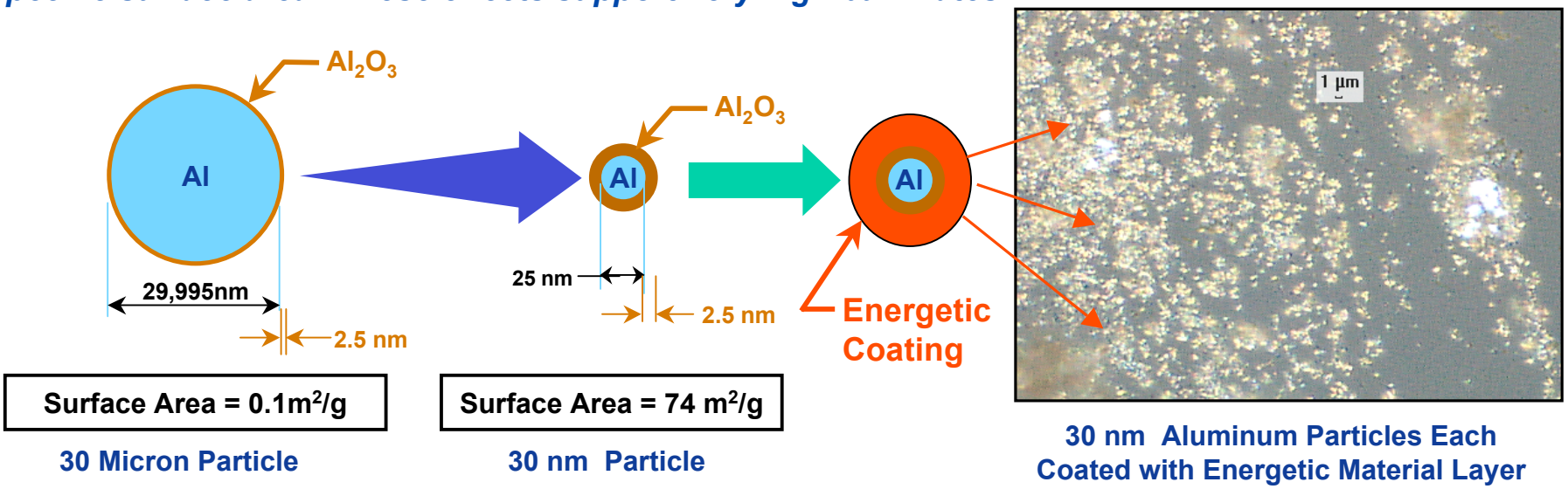


- **Conceptual and Experimental Breakthroughs**:
- **Molecules and assembly methods already conceptualized for building spin arrays with large variations in properties**
- **Recent experiments demonstrate the first possible example: an array of electron spins via e^- injection in self-assembled conjugated molecules**
- **Single spin magnetic resonance force probes are nearing operation (Marohn, Cornell) for addressing spin centers**

- **Opportunity**: **Utilize the powerful methods of molecular synthesis and self-assembly to form wide ranges of self-organized arrays of molecules with nuclear and/or electronic spin centers**

Nanometric Energetic Materials Research at AFRL Munitions Directorate

New approach for energetic materials: nano-thick energetic material coating-layer on nanoscale aluminum fuel particles gives improved, intimate mixing in energetic formulations, and very high specific surface area. These effects support very high burn rates.



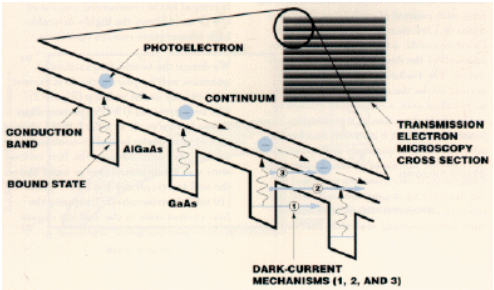
- *Scale Differences…*
  - Very High Specific Surface Area
    - 4- 6 Orders of Magnitude Increase
  - Short Diffusion Path-Length in Burning
- *… Can Lead to Important Performance Enhancements*
  - Complete Burning of Fuel Particles
  - Accelerated Burn Rates
  - Ideal Detonation in Fueled Explosives

- *Coating Benefits…*
  - Intimate Contact Between Fuel, Energetic Material
  - Fewer Problems with Processing, Handling
  - Material Coating Thickness on Nano-fuel Particles Is Nano-scale
    - Fewer Defects, Better Crystals
    - Improved Insensitivity Properties

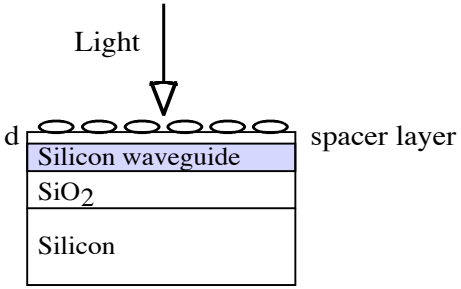
Quantum Well IR Sensors

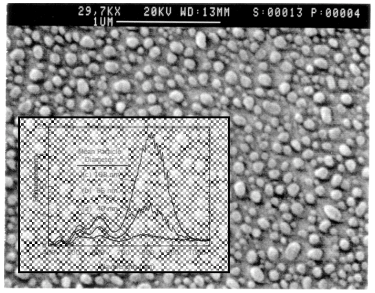
- Advanced Photodetectors
  - Quantum Well Infrared Photodetectors
    - Use electronic band engineering and nanofabrication techniques
    - Multispectral IR imaging
  - Uncooled Infrared Detectors
    - Uses nanofabrication and advanced materials
  - Nanoparticle-Enhanced Detection
    - Increase light detection by 20X
- Target Designation and CCM
  - IR Lasers for Target Designation
    - Need: Compact, 300K IR lasers
    - Solution: Quantum cascade lasers
- Impact on Future Army
  - Smart, multispectral sensors coupled with ATR for target ID
  - Shorter logistics tail

Quantum Well Infrared Photodetectors



Nanoparticle Enhanced Detection





AH-64 Apache

Hellfire

REACTIVE METAL OXIDE NANOPARTICLES FOR SOLDIER PROTECTION

Research Objective: Synthesis, characterization, and application of reactive metal oxide nanoparticles for protection against chemical and biological warfare agents and ballistic protection

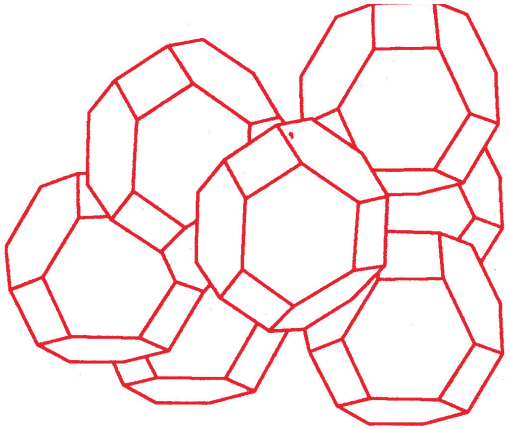
Transitions: ARO program supports Professor Ken Klabunde at Kansas State University collaborating with ECBC Next Generation Sorbent Decontamination Program(FY09), Domestic Preparedness Office at SBCCOM, Reactive Protective Skin Cream program at USAMRICD, PM for Nonstockpile Chemical Demilitarization, Ballistic protection programs at Natick Soldier Center.

R&D Partners: ARL-ARO/ECBC/NSC/USAMRICD/Universities/Industry

New Solutions for Decontamination and Protection of the Soldier in a Chemical and Biological Warfare Environment

—Surface area	MgO
Commercially Available	$30m^2$
Reactive Nanoparticles	$500m^2$

•High Surface Area with increased reactivity



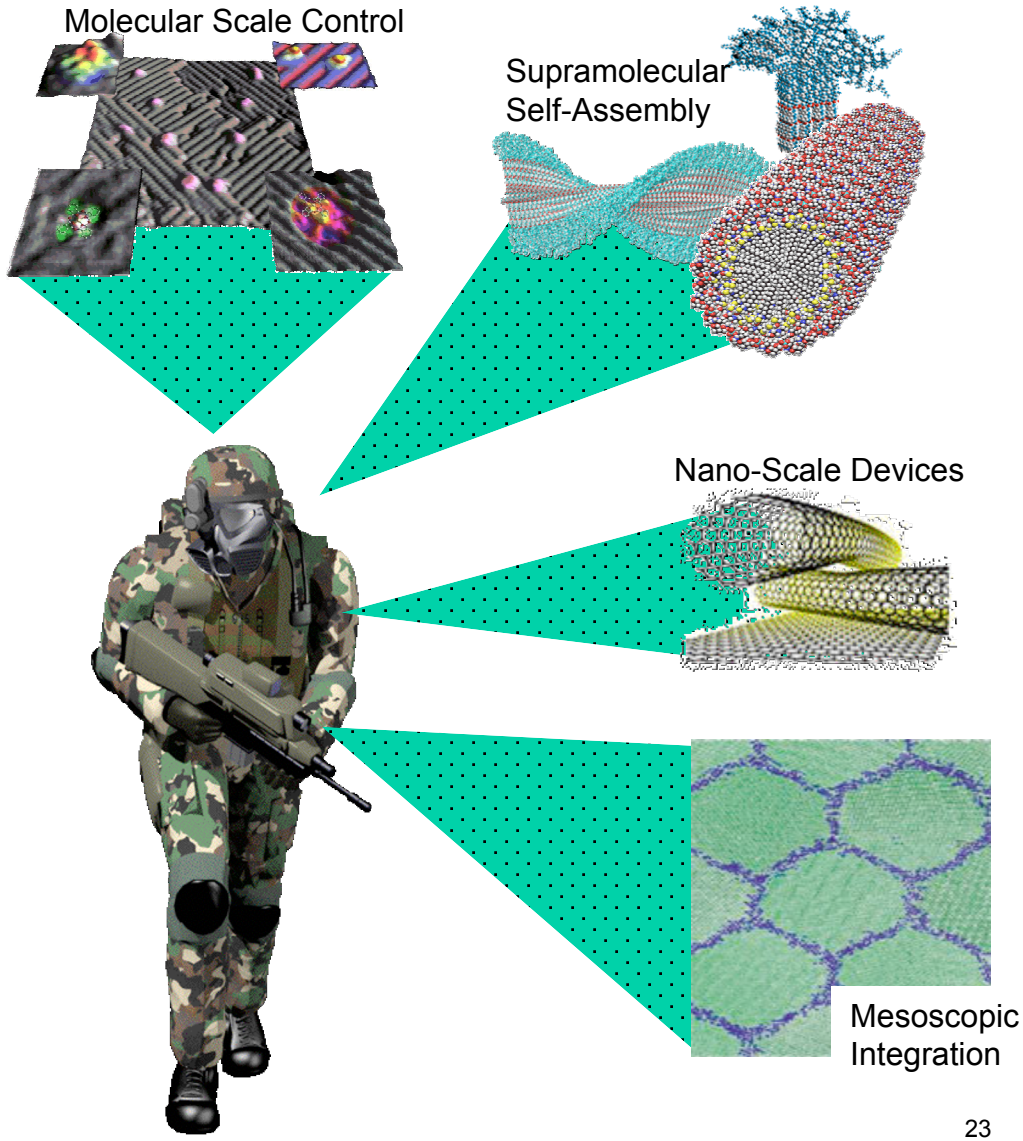
Payoff: Highly effective enhanced reactivity for the degradation of chemical and biological agents with reduced materiel burden. Enhanced Ballistic Protection for the soldier.

Institute for Soldier Nanotechnologies
MIT

University Affiliated Research Center
- Investment in Soldier Protection
- Industry partnership/participation
- Accelerate transition of Research Products

Goals
- Enhance Objective Force Warrior survivability
- Leverage breakthroughs in nanoscience & nanomanufacturing

Investment Areas
- Nanofibres for Lighter Materials
- Active/reactive Ballistic Protection (solve energy dissipation problem)
- Environmental Protection
- Directed Energy Protection
- Micro-Climate Conditioning
- Signature Management
- Chem/Bio Detection and Protection
- Biomonitoring/Triage
- Exoskeleton Components
- Forward Counter Mine



Summary

- Nanoscience/nanotechnology remains one of the top priority research programs within DoD
- Nanotechnology will impact practically all arenas of warfighting
- Potential for payoff to DoD is great, and is worth the investment