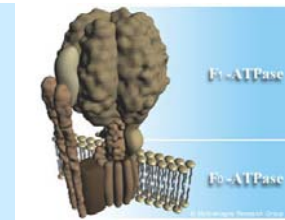




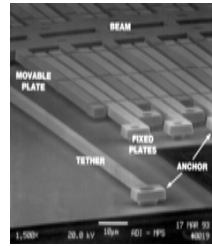
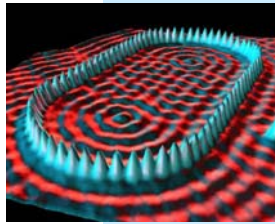
**Status Report on the (various) National Nanotechnology Initiative(s)
Industrial College of the Armed Forces
March 6, 2003**

**Dr. James S. Murday
Head, Chemistry Division, Naval Research Laboratory
Director, National Nanotechnology Coordination Office**

NANOMETER (nm) SCIENCE AND TECHNOLOGY



MAT - TECH



INFO - TECH

pm



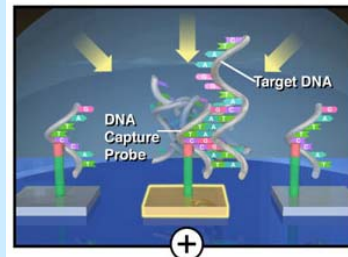
nm

μ m

mm

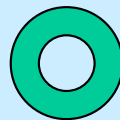
meter

km

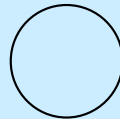


BIO - TECH

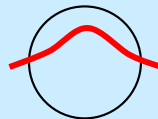
PHENOMENA



Interface/Interphase



Size effects



Quantum confinement

EXAMPLE

oxide layer

cell membrane

paramagnetic limit

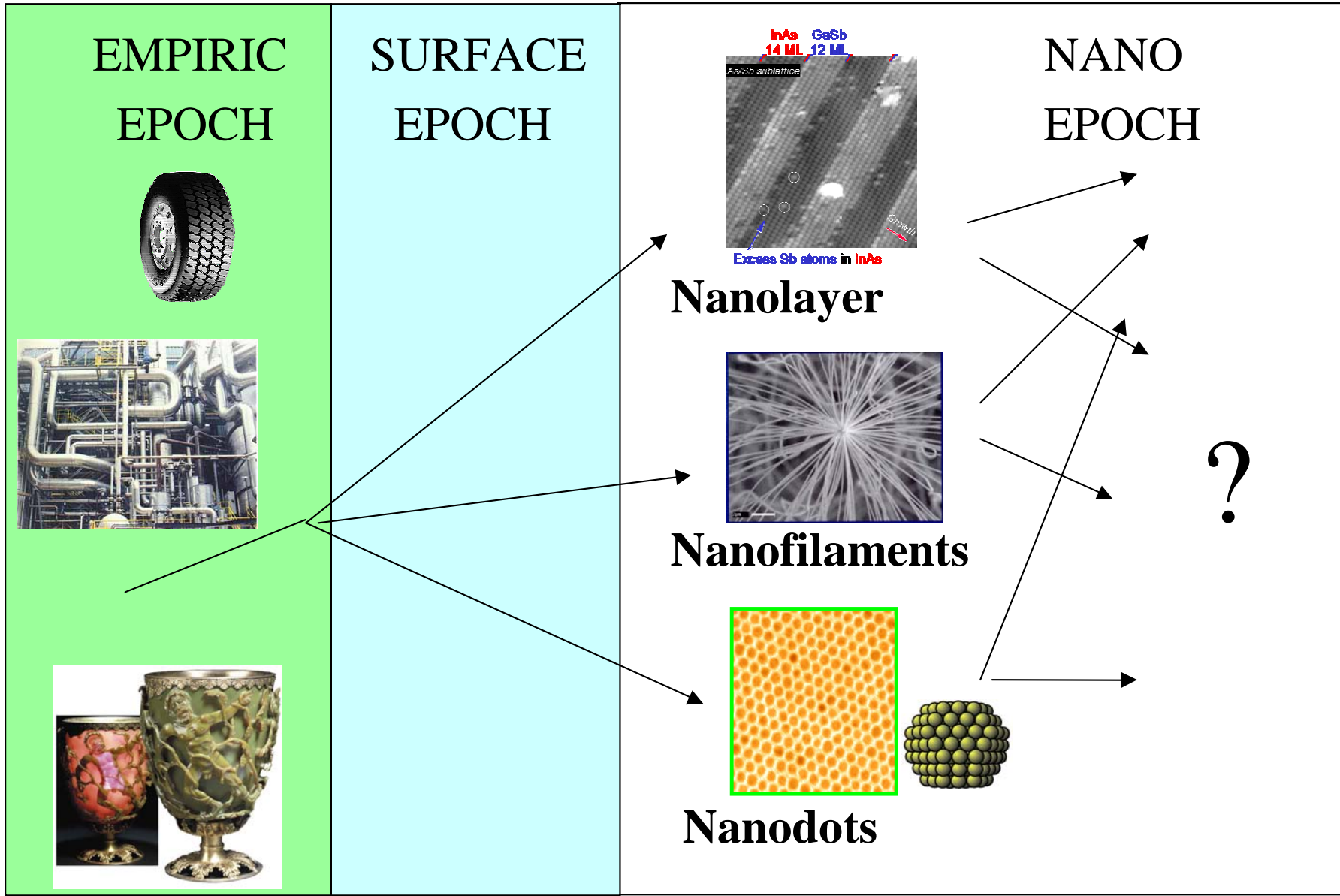
antibody/antigen recognition

QD color



Single electron device

Paleontology of Nanostructures



1960

1990

NANOTECHNOLOGY

Potential Economic Impact in 15-20 years: **“NANO INSIDE”**

Estimates by various Industry Representatives

\$340B Materials	materials, processing
\$300B Electronics	“nanoelectronics”
\$180B Pharmaceuticals	1/2 of production
\$100B Chemical Manufacture	catalysts
\$70B Aerospace	
\$20B Tools	automation, life cycle cost
\$30B Improved Healthcare	tools for healthcare
<u>\$45B Sustainability</u>	<u>agriculture, water, energy</u>

~\$1T Total

NanoBusiness Alliance
CMP Cientifica

www.nanobusiness.org/
www.cmp-cientifica.com/cientifica/frameworks/generic/public_users/NOR/NOR.htm

Roco, NSF

“NANOTECHNOLOGY” RESEARCH PROGRAMS IN THE WORLD

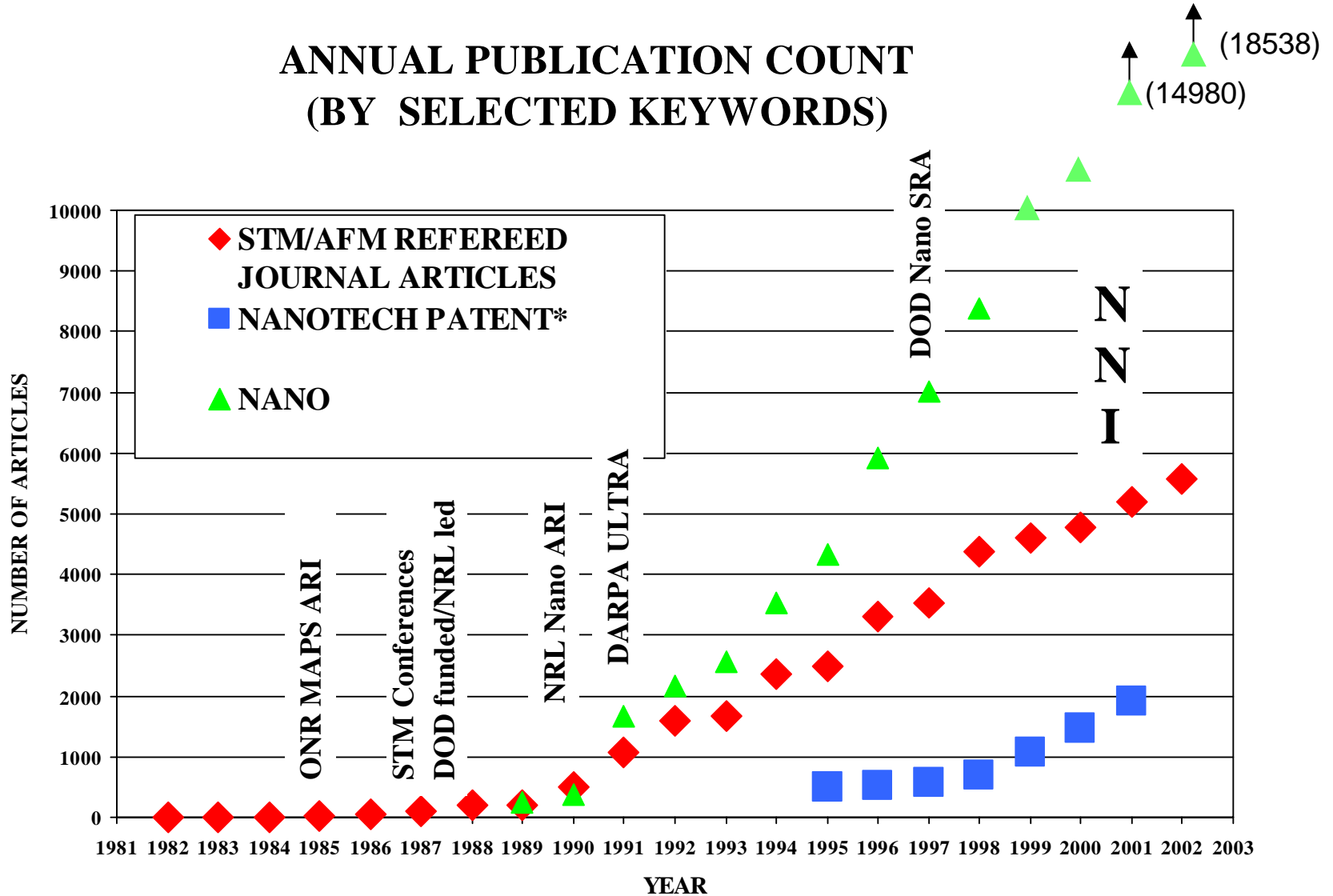
Main government sponsored research programs

	~1997 (WTEC)	2001	2002 (est)
USA	\$115M	\$420M	~\$700M
JAPAN	\$120M	\$500M	~\$800M
WESTERN EUROPE	\$125M	\$250M	~\$300M
OTHER COUNTRIES (FSU, China, Canada, Australia, others)	\$ 70M	\$200M	~\$400M
TOTAL	\$430M	~\$1400M	>\$2000M

Fiscal year start/stop varies from country to country

Return on Basic Research Investment: Nurturing Nanoscience into DoD Nanotechnology

ANNUAL PUBLICATION COUNT (BY SELECTED KEYWORDS)

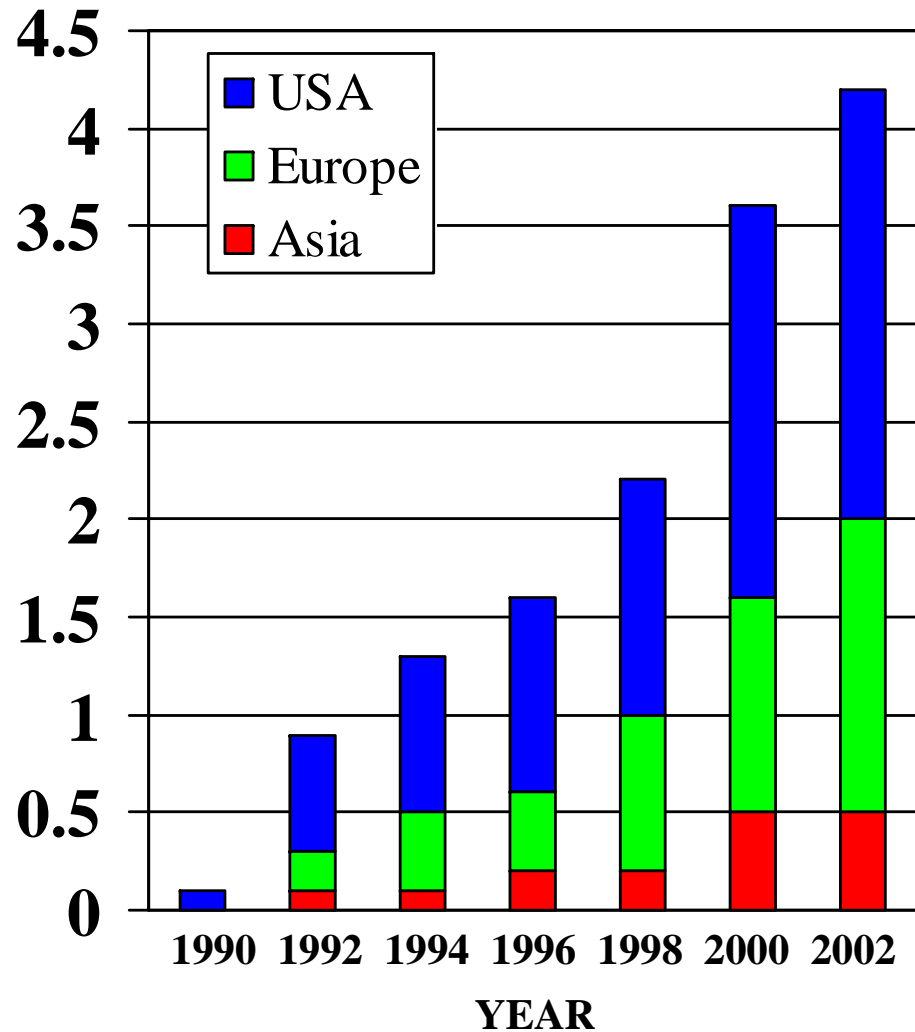


* "Nanotechnology – Size Matters", white paper, 10 July 2002, Institute of Nanotechnology

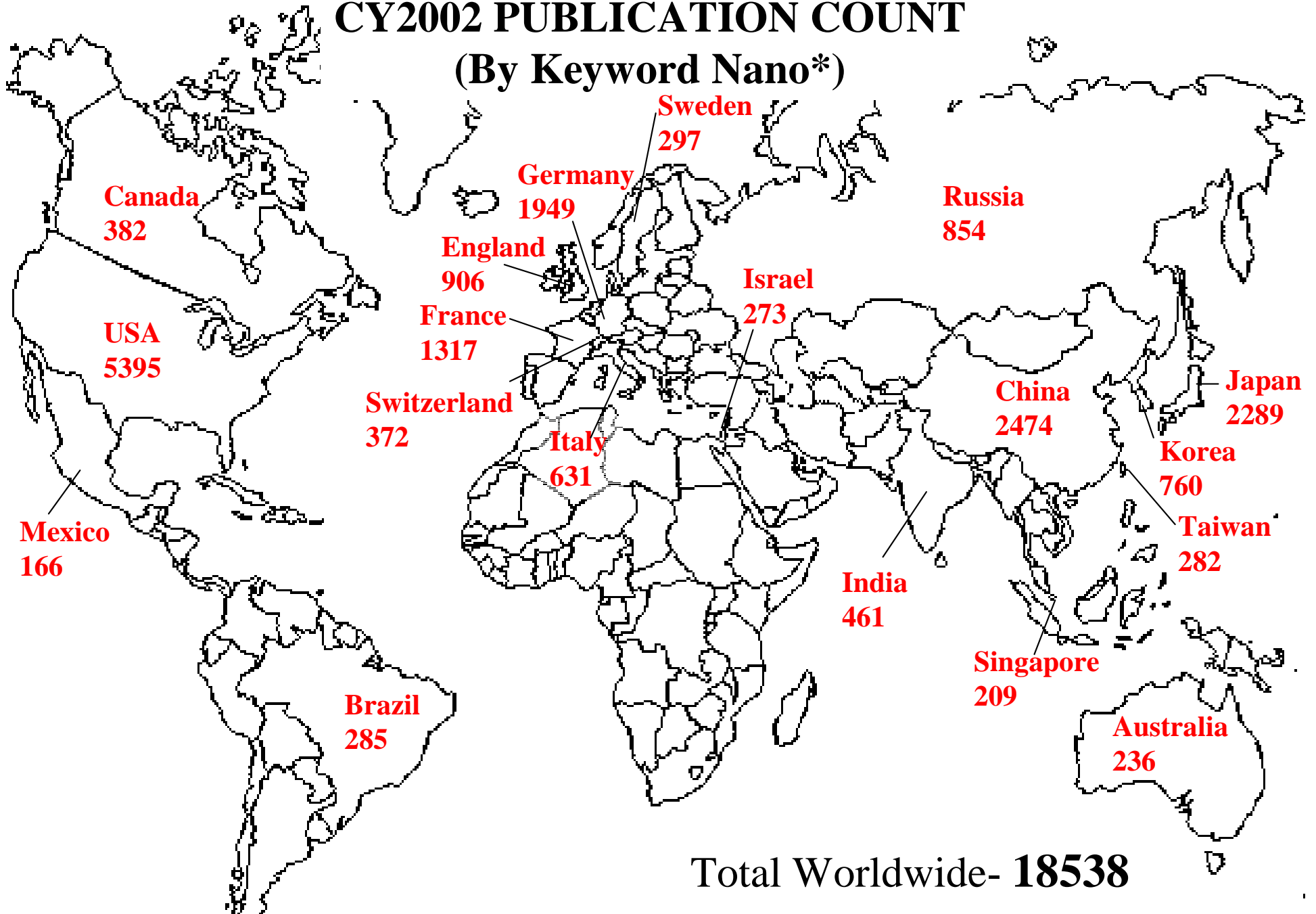
Journal ISI Impact Factors (2001)

Nature	27.9
Science	23.3
Phys Rev Lett	6.6
Appl Phys Lett	3.8
Prog Polym Sci	3.7
Macromolecules	3.7
Chem Matl	3.6
J Phys Chem B	3.3
J Chem Phys	3.1
Phys Rev B	3.0
Phys Rev A	2.8
J Matl Chem	2.7
Chem Phys Lett	2.3

Percentage of “Nano*” Articles in Nature/Science/PRL



CY2002 PUBLICATION COUNT (By Keyword Nano*)



US: NATIONAL NANOTECHNOLOGY INITIATIVE (NNI) PROGRAM (\$M)

		FY01	FY02	FY03	FY04
KNOWLEDGE GENERATION		152	212		
GRAND CHALLENGES		151	235		
NANOSTRUCTURED MATERIALS BY DESIGN	NSF		~55		
NANOELEC, PHOTONIC, MAGNETIC	DOD		~90		
ADVANCED HEALTHCARE/THERAPEUTICS	NIH		~20		
ENVIRONMENTAL IMPROVEMENT	EPA		~10		
ENERGY CONVERSION/STORAGE	DOE		~10		
MICROCRAFT & ROBOTICS	NASA		~5		
CBRE PROTECTION/DETECTION	DOD		~20		
INSTRUMENTATION & METROLOGY	NIST		~15		
MANUFACTURING SCIENCE	NSF		~10		
CENTERS/NETWORKS		71	89		
INFRASTRUCTURE		77	52		
ETHICAL/SOCIAL IMPLICATIONS		13	16		
	TOTALS	464	604	~775	~850

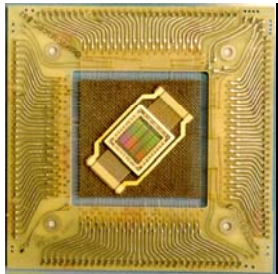
DoD Nanoscience Funding Summary

(\$M – “mainstream”)

	FY00	FY01	FY02		FY03 (est)		FY04 (rec)	
			6.1	6.2/6.3	6.1	6.2/6.3	6.1	6.2/6.3
Air Force	7	10	10	8	9	4	9	10
Army	6	6	18	4	22	7	20	10
Navy	21	31	37	3	30	1	28	1
DARPA	40	40	49	69	42	100	36	80
DDRE	15	36	26		28		28	
Total	89	123	224		243		223	

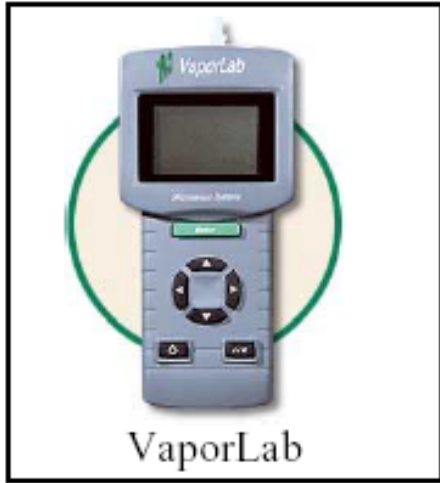
Enhanced warfighting capabilities

- * **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



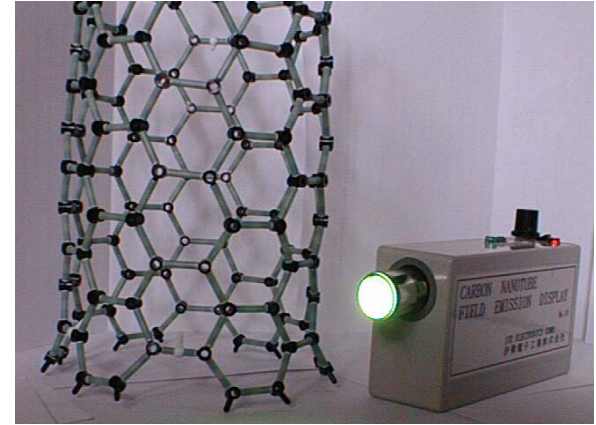
INFORMATION NANOTECHNOLOGY

AU Nanocluster Vapor Sensor;
Snow NRL, MSI/SAWTEK

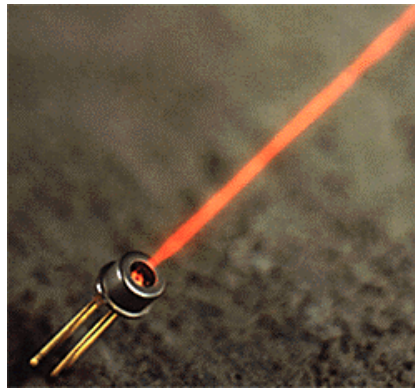


SENSE

DISPLAY



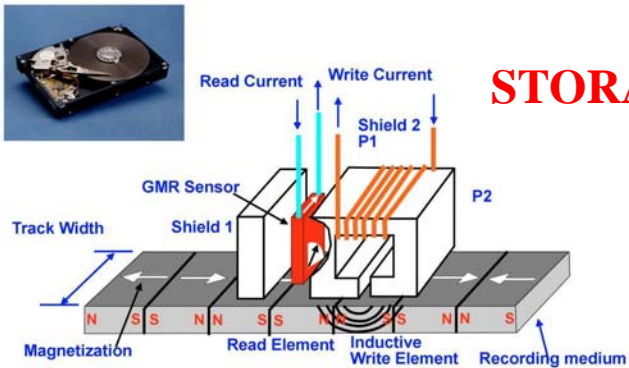
CNT FED Display; Zhou, UNC



TRANSMISSION

Superlattice VCSEL; Honeywell

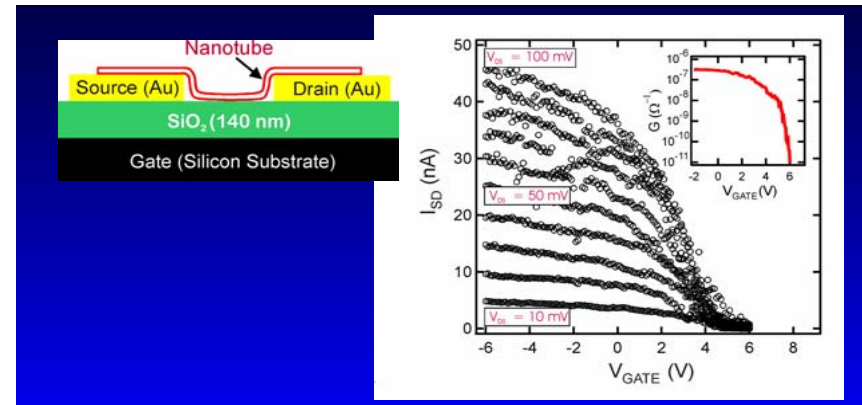
GMR Reading Head; IBM



STORAGE

Magnetic recording process.

LOGIC

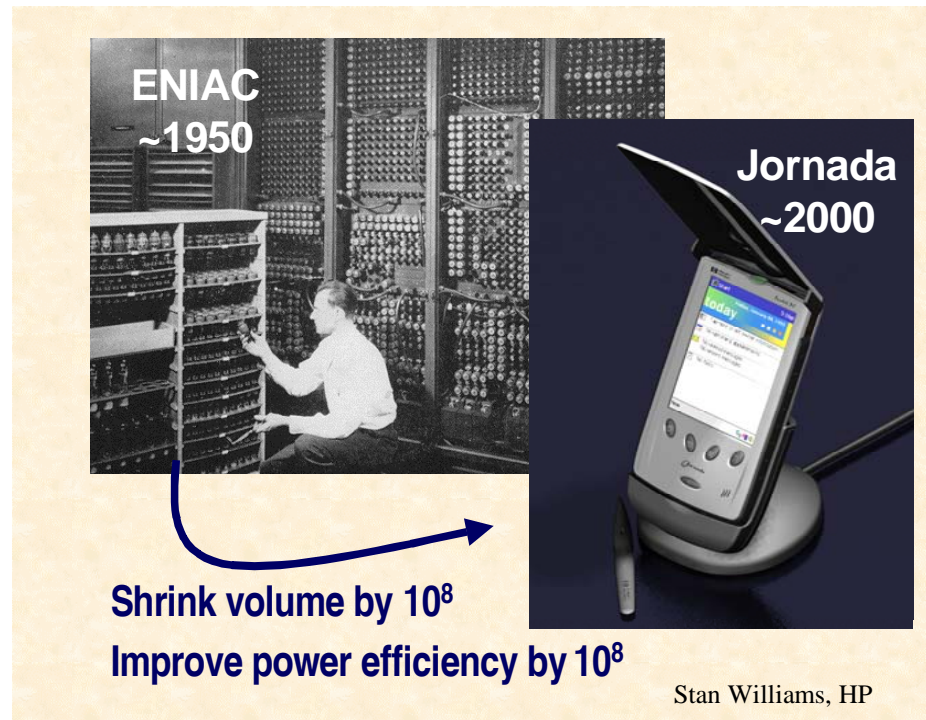


CNT FET; Avouris, IBM

Why Nanoelectronics?

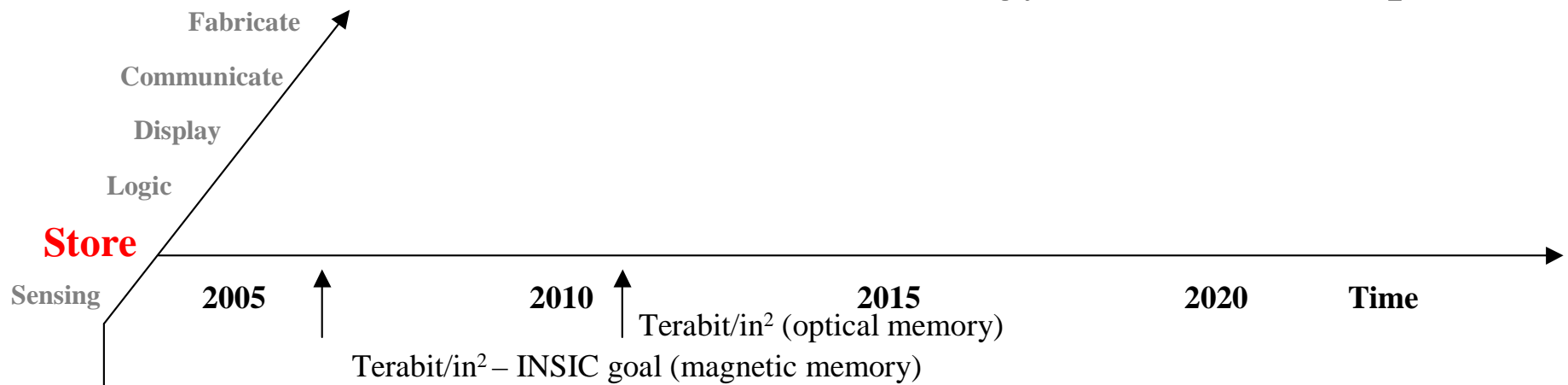
The evolution of computer technology over the last few decades has revolutionized computational capability

- Faster electronics
- Lower power consumption
- Larger data handling capabilities
- More complex information processing



The era of Nanoelectronics (<100 nm) is forecast (ITRS) to begin within 3 years (2005)

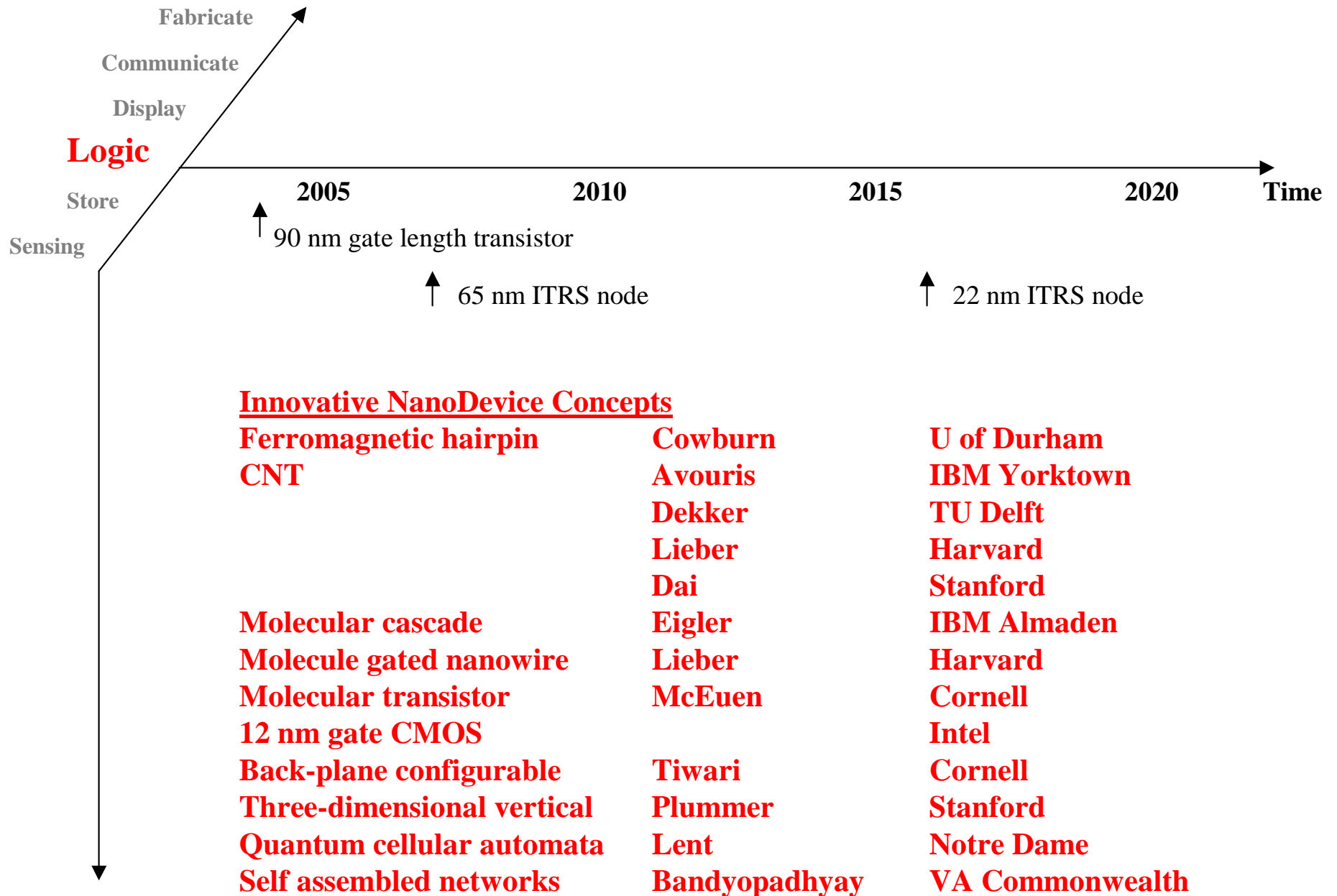
Information Technology NanoDevice Options



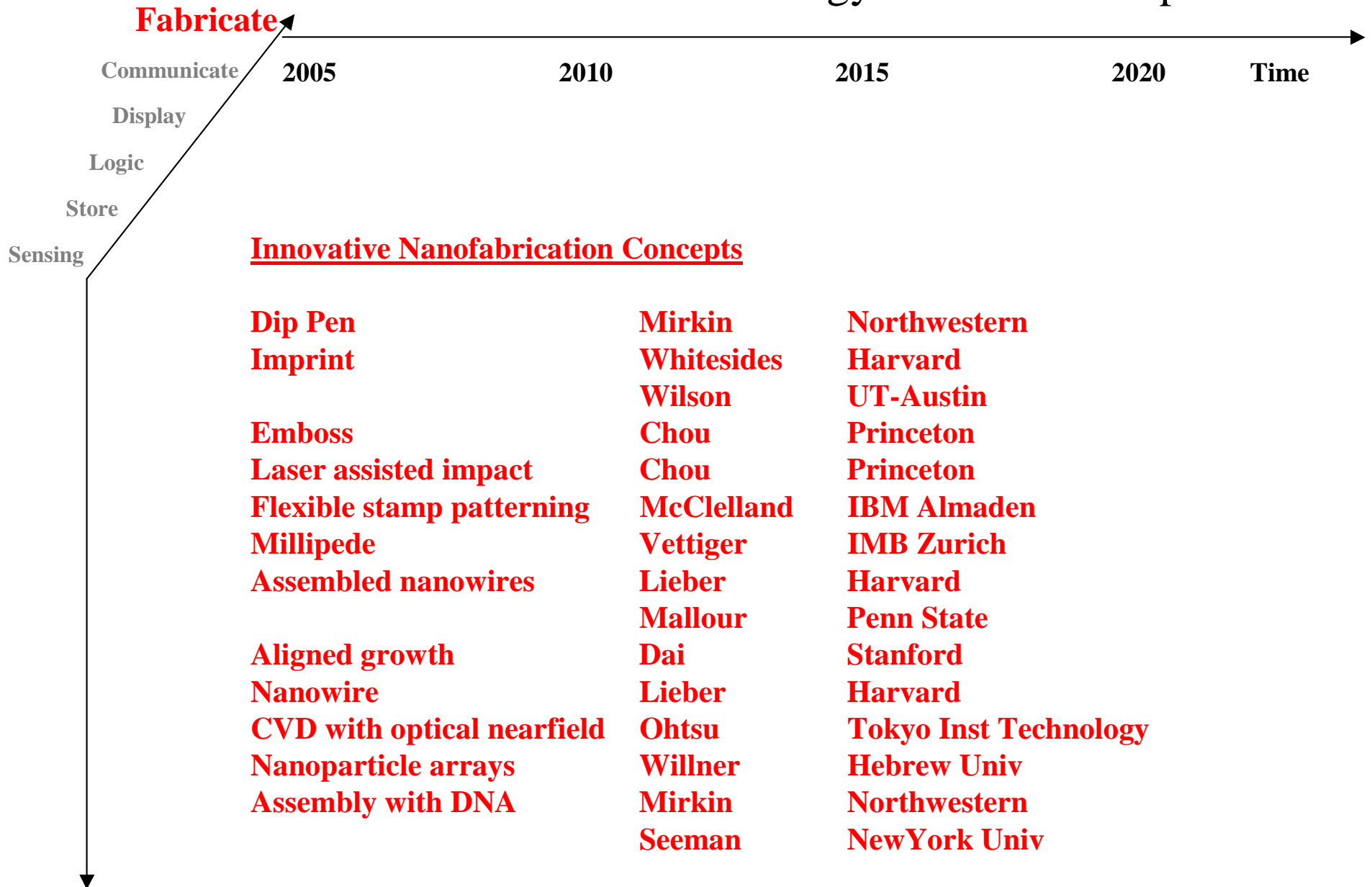
Innovative NanoDevice Concepts

Magnetic rods	Chou	Princeton
Magnetic nanocrystal	Sun	IBM Almaden
NanoCrystal memory	Tiwari	Cornell
Plastic deformation	Vettiger	IBM Zurich
Molecular switch	Heath	CIT
CNT switch	Lieber	Harvard
Ag₂S switch	Aono	RIKEN
GMR	Prinz	NRL
QD charge storage	Quate	Stanford
Back storage	Tiwari	Cornell
Ballistic magnetoresistance	Chopra	SUNY Buffalo
Molecular (64 bit)	Williams	HP
Heat assisted magnetic recording	Schlesinger	CMU
Near-field “apertures”	Schlesinger	CMU
Nanophotonics	Ohtsu	Tokyo Inst Technology

Information Technology NanoDevice Options

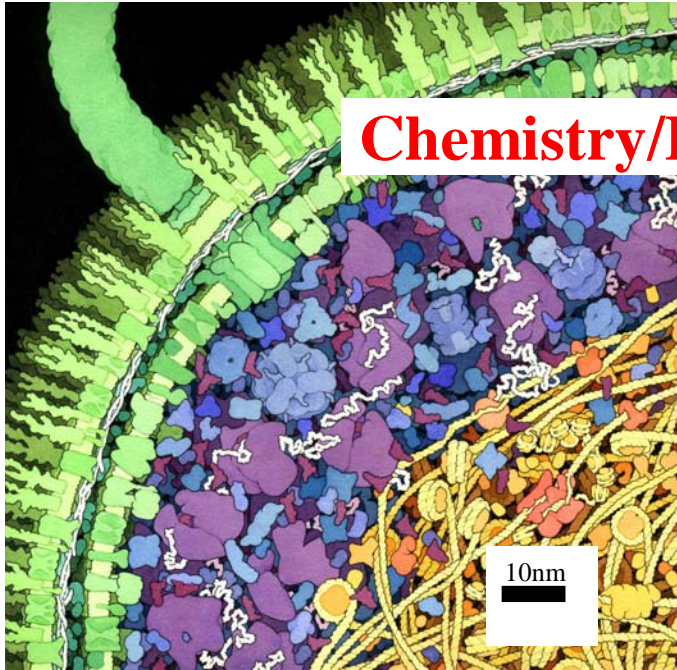


Information Technology NanoDevice Options



NANOBIOTECHNOLOGY

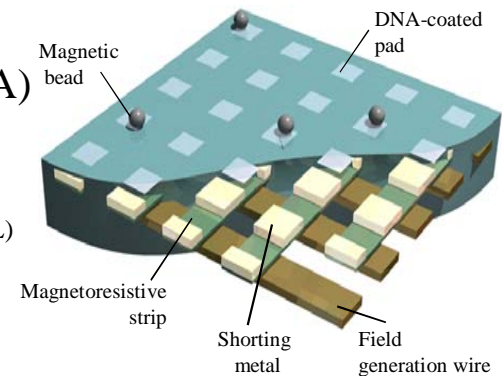
Chemistry/Physics of Biological Nanostructure



Small portion of an *Escherichia coli* cell
(Goodsell, Scripps; Sigma Xi 1999)

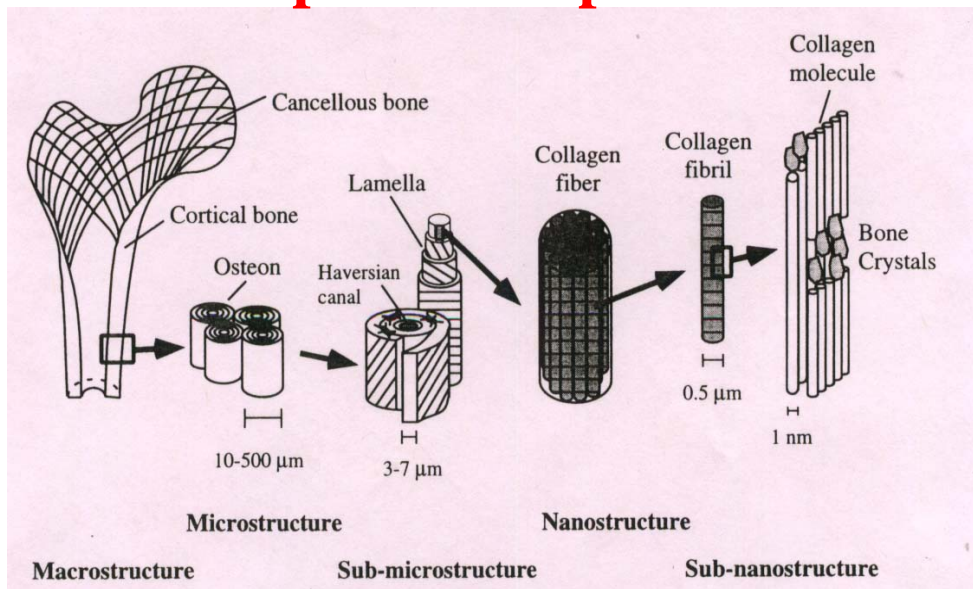
Earlier Detection and Treatment of Disease

Contrast Agents for Imaging
Sensors
Susceptibility Testing (DNA/RNA)



BARC Sensor (Colton, NRL)

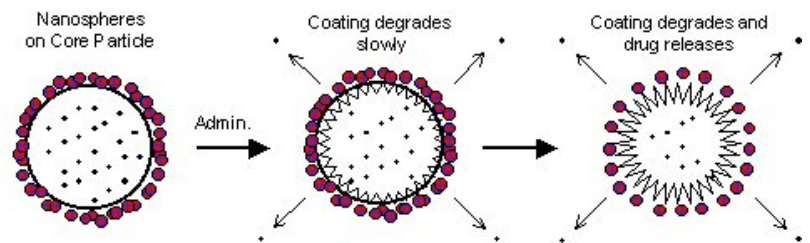
Improved Implants



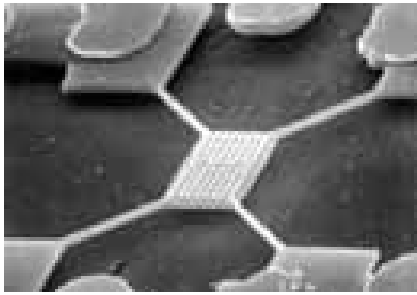
Bone Structure (Siegel, RPI)

Therapeutic Delivery

Enhanced Solubility
Targeted, Local Delivery

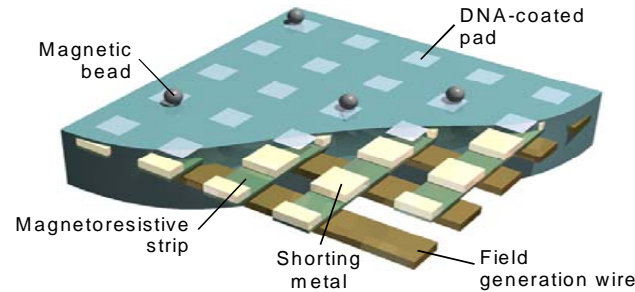


Nanosphere enhanced drug solubility
(Nanosphere)

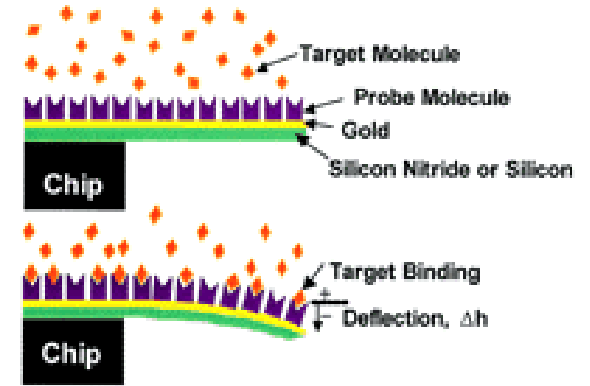


Nanocalorimeter; Roukes CIT

Why Nanostructures for Sensing



GMR Biosensor; Whitman/Prinz, NRL



Cantilever Sensor; Thundat ORNL

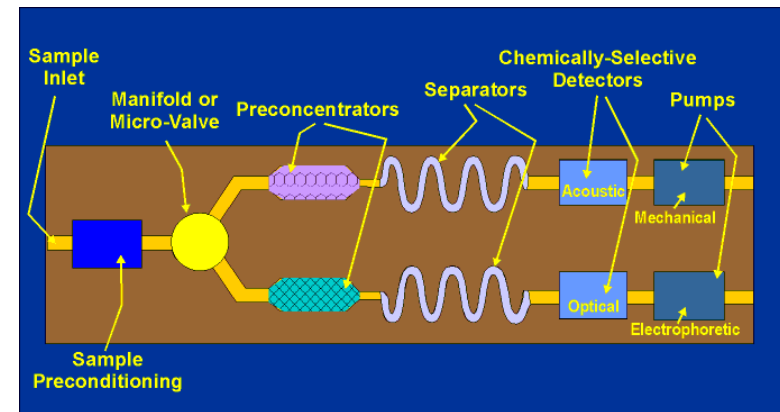
•Signal to noise improvements:

yocto(10^{-24})joule,

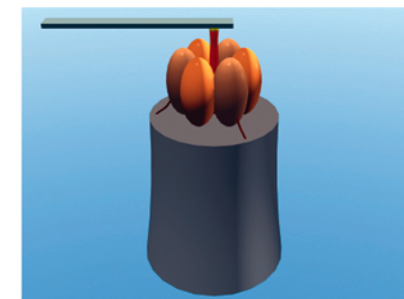
atto(10^{-18})newton,

single molecule,

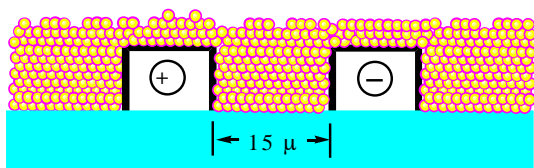
- Miniaturization – size/weight - arrays
- Lower power, potentially scavenged
- Locally process data into information



Lab-on-a-chip; Sandia

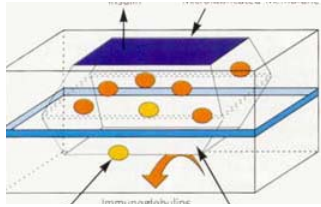


Molecular Motor; Montemagno Cornell



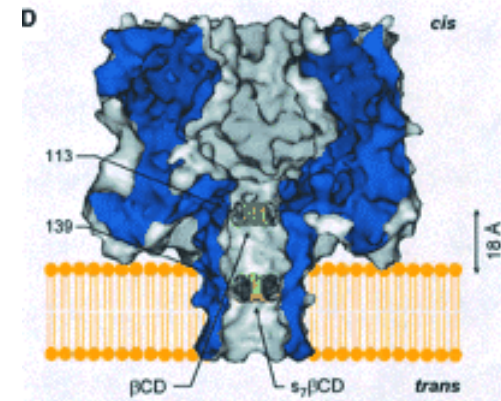
NanoAu Chemiresistor; Snow NRL

Why Nanostructures for Protection/Neutralization

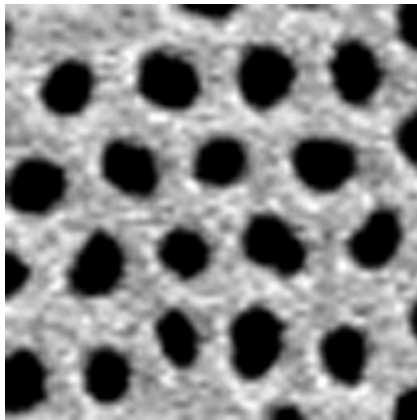


MEMS capsule, Desai

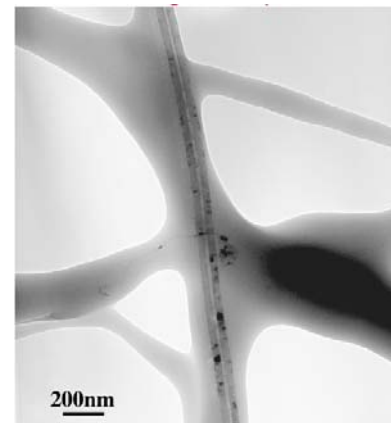
- High surface to volume ratio
- Porosity for separation
- Nanofibers for membranes, clothing
- Multiple reactive sites for catalysis/adsorption
- Disrupt physiological function
- Hierarchical assembly for multifunction



Cell membrane transport, Bayley



Nanopore Al, Martin



CNT in Electrospun Polyurethane, [Schreuder- Gibson](#)

Homeland Defense

Expected Impact of Nanotechnology

Lighter, smaller, and highly functional sensing systems that provide rapid, accurate, low cost detection
distributed surveillance “platforms” for buildings, transportation hubs,...
uninhabited vehicles for response teams to reduce the risk to human lives.
personnel monitors for CBRE threats, physiological fatigue, medical applications

Protective clothing that incorporates decontamination activity rather than simple adsorption, and permits water vapor migration for cooling.

Masks/filters with adsorbents having greater selectivity and capacity for harmful agent, incorporating miniaturized sensing to detect breakthroughs, and potentially neutralizing the agent.

Decontamination more benign to humans and environment

Innovative approaches to the **deactivation of biological agents**, especially spores

Manufacturing and processing industries **free of hazardous materials and wastes**

NANOMATERIALS



Q-Dot Contrast Enhancers; Frankel, MIT

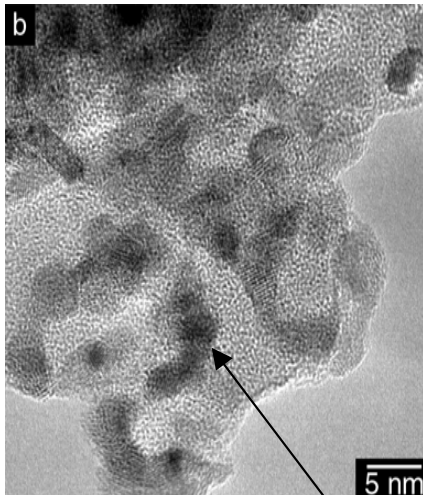


Netshape Formed Nanoceramics; Siegel, RPI

NANOSTRUCTURES

CONSOLIDATED NANOSTRUCTURED MATERIALS

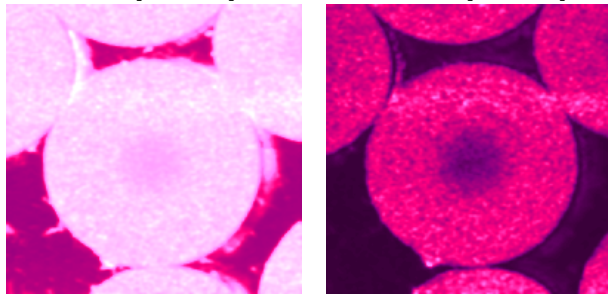
NANOCOMPOSITES



Nanocrystalline RuO₂ wire in Silica Aerogel; Rolison, NRL

E' (GPa)

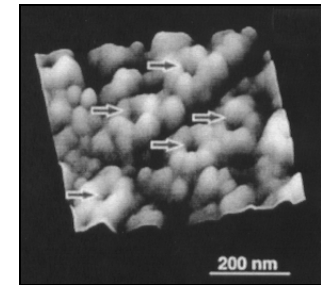
E'' (GPa)



10 μm

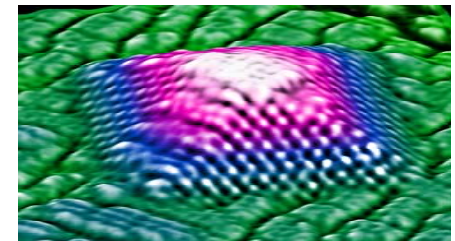
10 20 30 40 50 60 70 GPa

Composite Moduli Measurement; Wahl, NRL



Cell Membrane; Oberleithner, Münster

NANOPOROUS MATERIALS



DIRECTED SELF ASSEMBLY

NANOTECHNOLOGY HAS THE REAL DOT.COM

Mechanical – ceramic, powder metallurgy

Pfund Condensation – metals, ceramics

Colloid Chemistry

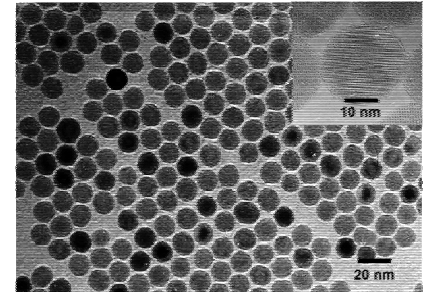
Chemical Precipitation – metals, intermetallics, ceramics

Surfactants – stabilize, size control

Sol-Gel – ceramics (oxides), porosity

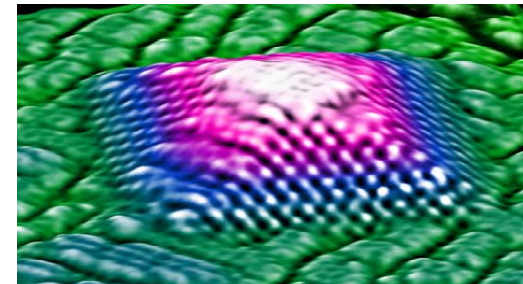
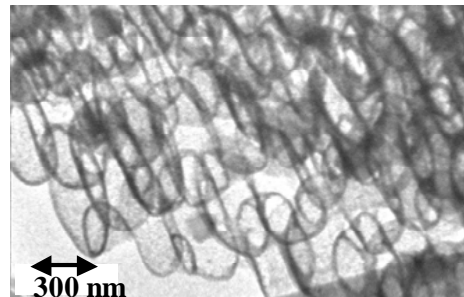
Strained Layer Growth

Molding



$\gamma\text{-Fe}_2\text{O}_3$ Nanocrystallites
(J.Am. Chem. Soc., 123, 12798 (2001))

Nanomolded polymer
(Colvin, Rice)



GE Self Assembled Pyramid on Si.
10nm at Base
(S. Williams, HP)

NANOTECHNOLOGY IS WIRED FOR SUCCESS

Catalytic Growth

Laser assisted:

III-V, II-VI, IV-IV - GaAs, GaP, InP, InAs, CdS, $\text{Si}_{1-x}\text{Ge}_x, \dots$

Gas transport:

CNT, MoS_2 , WS_2 , BN, NiCl_2 , SiO_2 ,

Laser ablation:

Si

Self Assembly

Surfactant assisted:

Cu, Zn, Cd - sulfides, selenides

Amphiphilic

lipids

Template

Pore filling:

metals, polymers, semiconductors, carbons

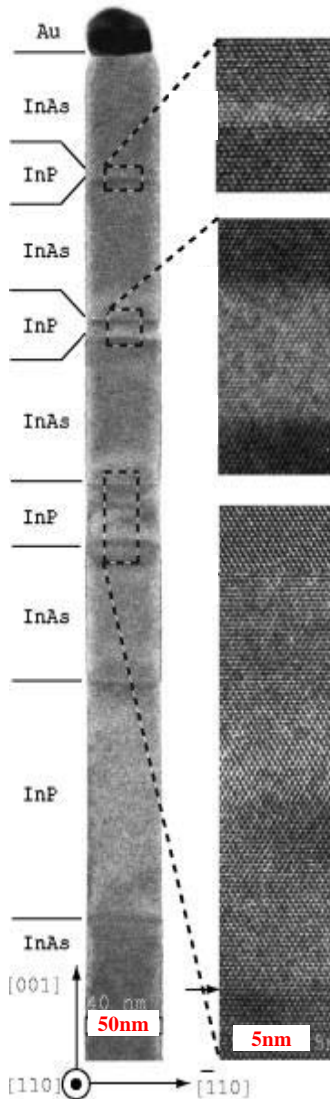
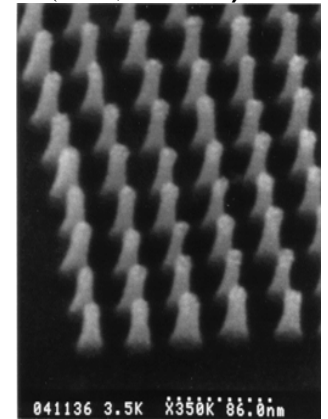
Edge decoration:

Mo

Stressed Thin Films

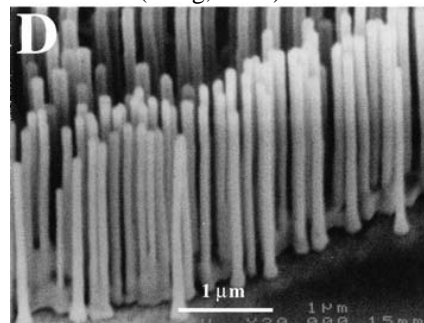
SiGe

10 nm dia. SiO₂ Mold
(Chou, Princeton)



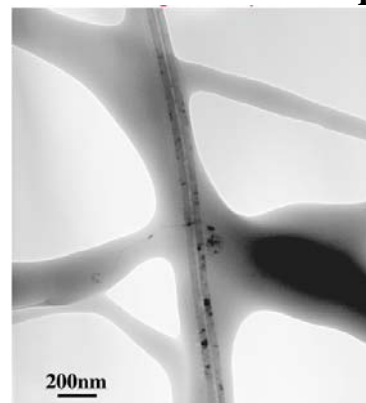
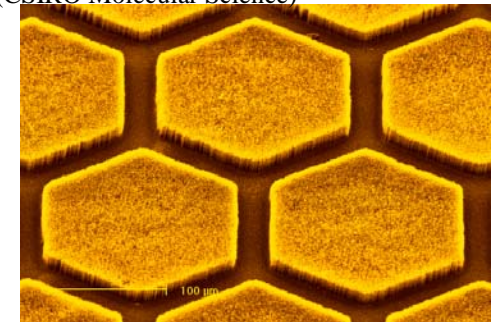
Nanowire Superlattice
(Samuelson, Lund)

ZnO nanorod
(Yang, UCB)



Patterned carpets of aligned carbon nanotubes

(CSIRO Molecular Science)



10% CNT in Electrospun Polyurethane
(Schroeder-Gibson, Natick Soldier Center)

Nanotechnology: When it Reigns, it Pores

Ion track etch

Anodized films

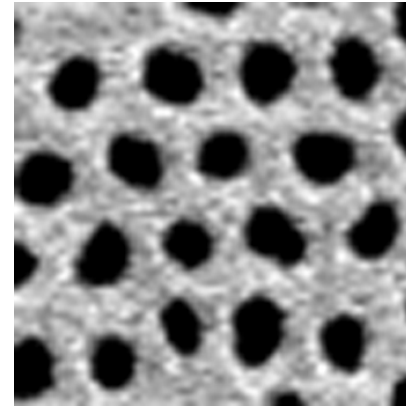
Surfactant aided “self-assembly”

Drawn glass-fiber nanochannels

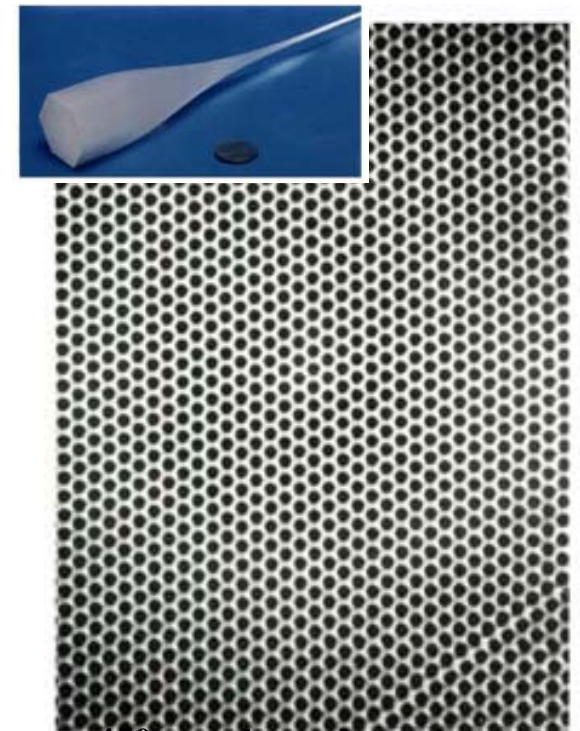
NEMS/MEMS

Crystallization with small pores – zeolites,...

Sol/Gel – aerogel, xerogel, ambigel

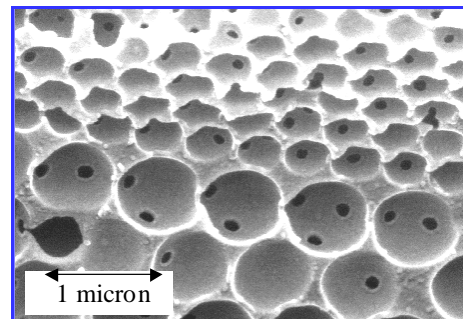


Nanopore Alumina
(Martin, Univ of FL)



450-nm channels

Macroporous polymer
(Colvin, Rice)



Nanochannel glass
(Tonucci, NRL)

Directed, Hierarchical “Self”-Assembly of Nanostructured Systems

Directed

Surface/Interface

strained layer overgrowth

graphoepitaxy

Patterning

embossing

printing

dip-pen

Recognition

hydrophobic/hydrophilic

biological – DNA, Antibody/Antigen

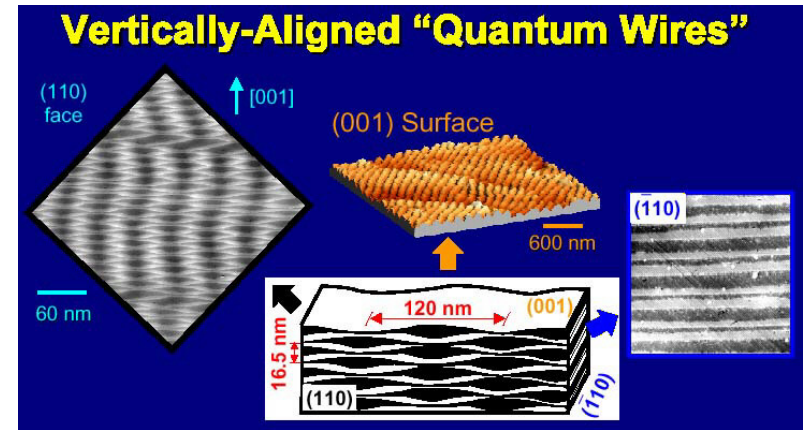
“Self”-Assembly

direct growth

flow oriented structures

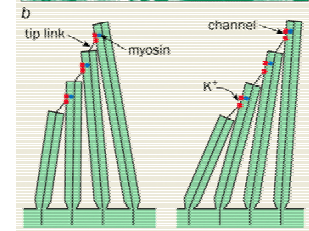
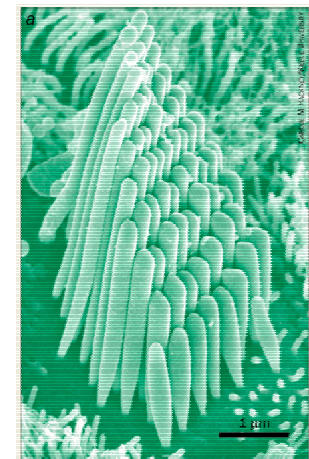
field oriented structures

Hierarchical

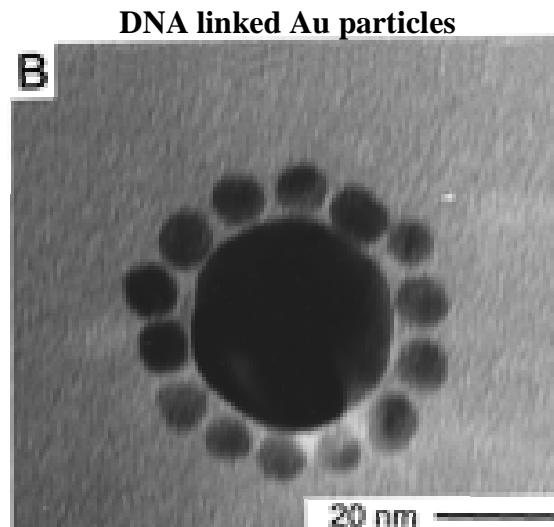


Whitman, NRL

Nanorod bundles in ear



Physics World, May 2002



Mirkin, Northwestern

NANOTECHNOLOGY – EARLY RETURN TO NAVY

EVOLVING SUCCESS STORY: NANOSTRUCTURED COATINGS

1981: Gleiter initiates nanocrystalline metal science

1990: Science Base for nanophase materials begins to expand rapidly

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.

2001: R&D 100 Award

2002: Nano coating on U.S. Navy ship air intake/exhaust valve with estimates savings of \$20M over 10 years.

Dr. Lawrence Kabacoff and Dr. Asuri Vasudevan, ONR, co-winners of the Dual Use Science & Technology Achievement Award

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



Properties of Inframat Nano-Alumina/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/mm³)	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 cycle	>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

References.

1. Y. Wang, S. Jiang, M.Wang, S. Wang, T.D. Xiao, P.R. Strutt, "Abrasive Wear Characteristics of Plasma Sprayed Nanostructured Alumina/Titania Coatings," *Wear* **237** (2000) 176-185
2. R.W. Rigney, Presentation at ONR DUST Nanostructured Coating Program (ONR contract No. N00014-98-3-0005), Cape Code, May 17-19, 2000.
3. M. Gell, "Advanced Coating Technology Development for Enhanced Durability and Reduced Cost in Naval Application," ONR Contract No. N00014-98-C-0010, June 1997-Dec 2001.
4. T.D.Ciao, Y.Wang, S. Jiang, S. Wang, D.M. Wang, & P.R.Strutt, "Thermal Spray of nanostructured Alumina/Titania Coatings with Improved Mechanical Properties," *Procs. 2nd Intl. Conf. Surface Eng., Wuhan, China, Oct 17-22, 1999, pp12-146*

DOD VISIONS POTENTIALLY ENABLED BY NANOTECHNOLOGY

Warfighter System

Personal Information System - oral com, heads-up display, “map”, decision aids

Access to network, scavenged power

Monitor/actuation system for CBRN, fatigue

“Smart uniform” – camouflage, CB/ballistic protection

Virtual/Augmented Reality Training/Education/(Entertainment)

Full oral, visual, tactile interaction – tailored learning modes

Interactive group involvement

Electronic “paper” with conformal thin film power source

Uninhabited Combat Vehicle

Full image storage/processing in RF, mm, IR, visual, UV,...

Rapid (ms) decisions with “strategic” human intervention

High g maneuverability, low observable

CBRE Detection/Protection

Sensor suites with sensitivity and selectivity

Protective clothing/masks with decon capacity

Automated therapeutic responses

NNI Major Opportunities/Challenges

Marriage of biology and the nanoscale

“Second Industrial Revolution” vs Evolution hinges on:

Control and availability of affordable building blocks

Directed, hierarchical self-assembly

Environmental/human impact as quantities of nanostructures increase

Integration of world-wide activity

Nanotechnology becomes “mainstream” rather than “buzzword”

Determine appropriate NNI metrics