

**NANOTECHNOLOGY AND NANO
MATERIALS: TYPES, CURRENT/EMERGING
APPLICATIONS AND GLOBAL MARKETS**

Dr. Thomas Abraham

President

Innovative Research and Products (*iRAP*), Inc.

P.O. Box 16760, Stamford, CT 06905, USA

Tel: 203-569-7909

E-mail: tabraham@innoresearch.net

Web: www.innoresearch.net

Organization of the Presentation

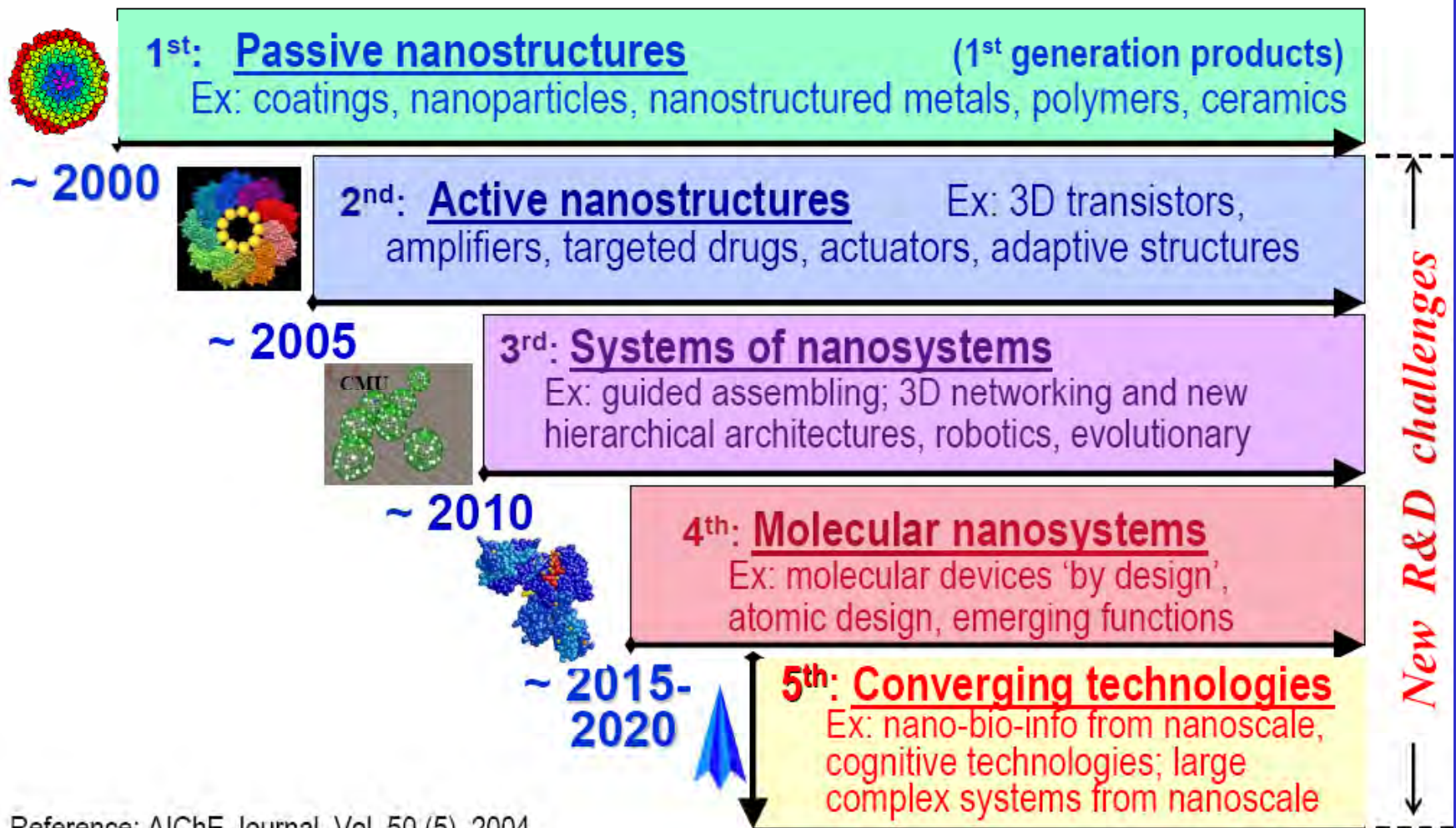
- Introduction
- Definition
- Nanotech Investment
- R&D Spending
- Nanomaterials
- Synthesis Techniques
- Nano Manufacturing
- Commercial Products
- Current Applications
- Next Generation Applications
- Global Markets
- Conclusions

Nanotechnology

- Working with these structures, one by one, or cluster by cluster to design and develop stronger & lighter materials, faster acting switches, drugs & cosmetics, more storage

Five Generations of Products and Productive Processes

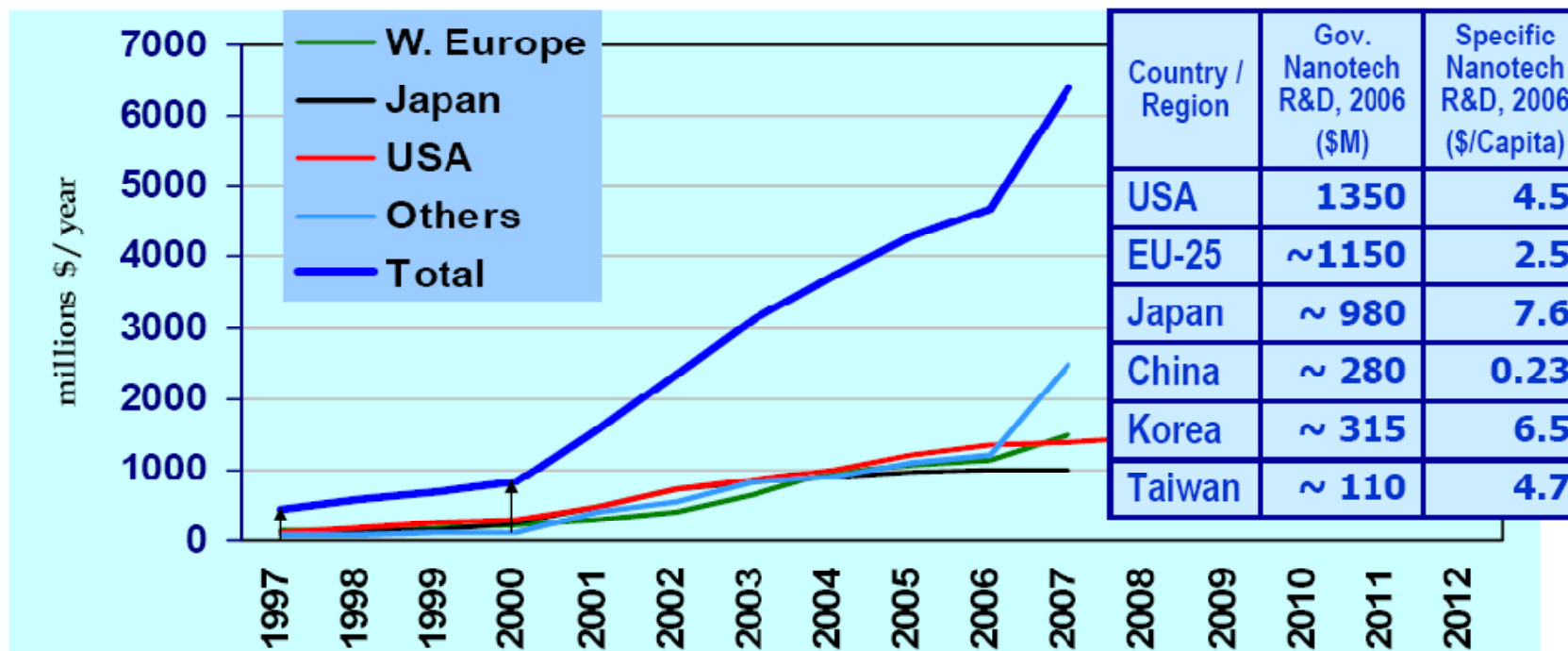
Timeline for beginning of industrial prototyping and nanotechnology commercialization (2000-2020; 2020-)



Reference: AIChE Journal, Vol. 50 (5), 2004

Context – Nanotechnology in the World

National government investments 1997-2006 (est. NSF)



Seed funding
(1991 -)

NNI Preparation
(vision / benchmark)

1st Strategic Plan
(passive nanostructures)

2nd Strategic Plan
(active ns. & systems)

Industry R&D (\$6B) has exceeded national government R&D (\$4.6B) in 2006

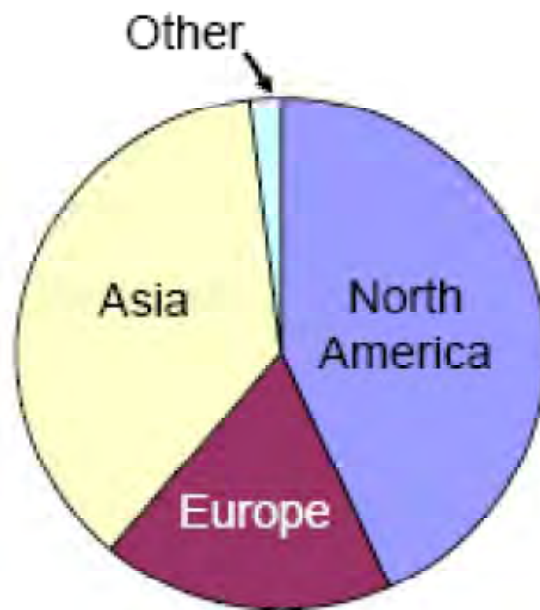
J. Nanoparticle Research, 7(6), 2005, MC, Roco

Innovative Research and Products, Inc.
www.innoresearch.net

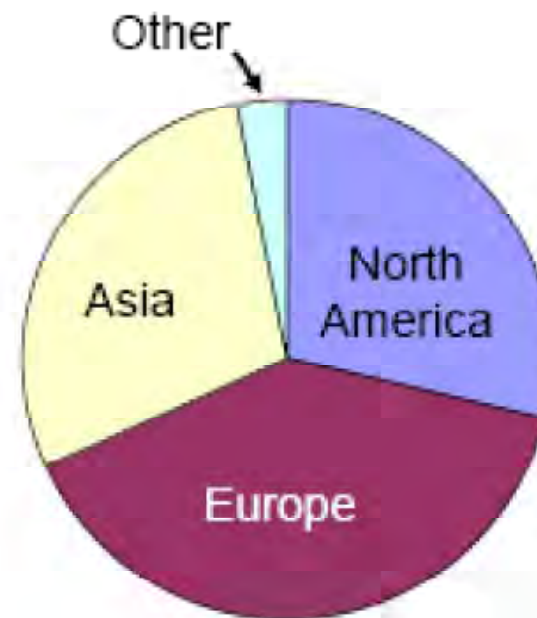
National Nanotechnology Initiative Budget 2006-2012 (Millions)

2006	-	\$ 1,351
2007	-	\$ 1,425
2008	-	\$ 1,554
2009	-	\$ 1,650
2010	-	\$ 1,913
2011	-	\$ 1,805 (Estimated)
2012	-	\$ 2129 (Proposed)

Growing nanotechnology R&D investment - \$12.6 billion in 2006



Private (Corp. + VC)
Total = \$6 billion



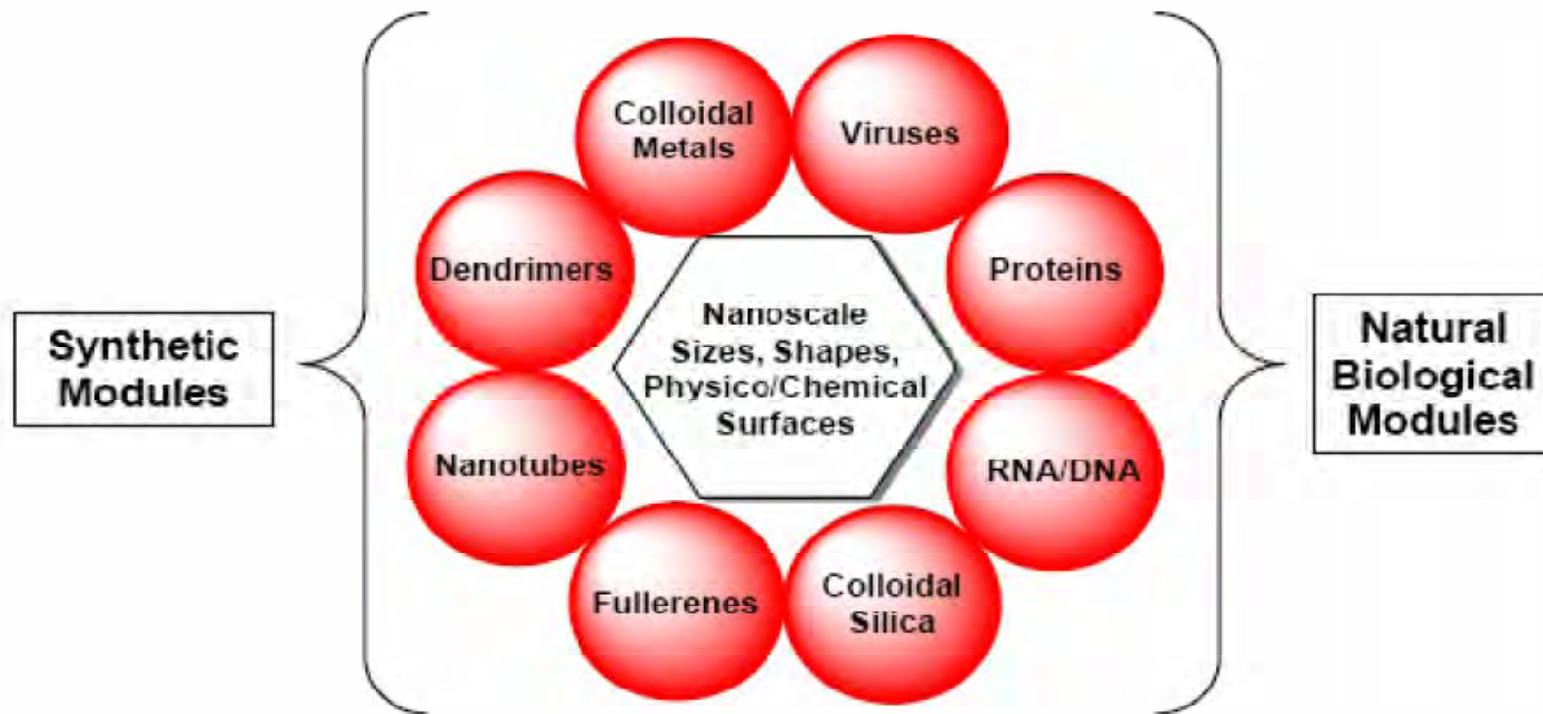
Public (National, regional, state)
Total = \$6.4 billion

Source: Lux Research

M.C. Roco, 2/23/2008

Natural and synthetic nanoscale modules / building blocks

(typical examples for first level of organization of atoms and molecules)



Basic challenges in nanotechnology: creating nanoscale modules, tools, exploiting new behavior, process control in nanomanufacturing

Workshop U. Mich, M.C. Roco, 2/23/2008

Nanomaterial Types

- Carbon black, carbon nanotubes, graphene, fullerene, nanofibers
- Silica fumes
- Clay
- Metal/alloys
- Ceramics

Used in tires /rubber products, fillers, pigments, semiconductors, electronic components, pharma additives, synthetic bone, polishing slurries, sunscreen lotion and polymer composites.

Synthetic Strategies

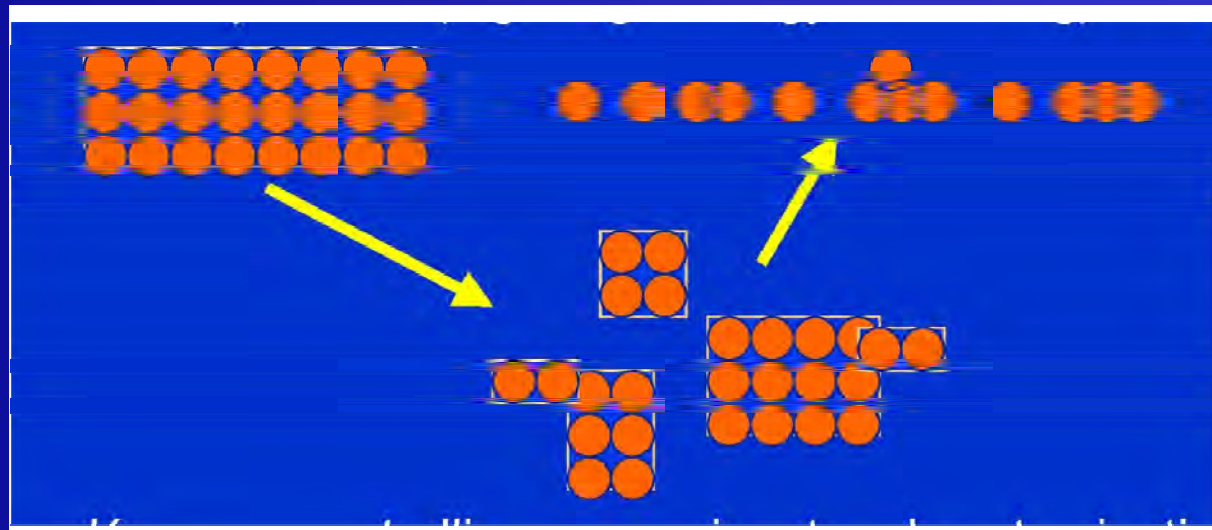
Top → Down

Bulk particulate materials are broken down into smaller and smaller particles

Process key – control energy input and contamination

Example – high energy ball milling

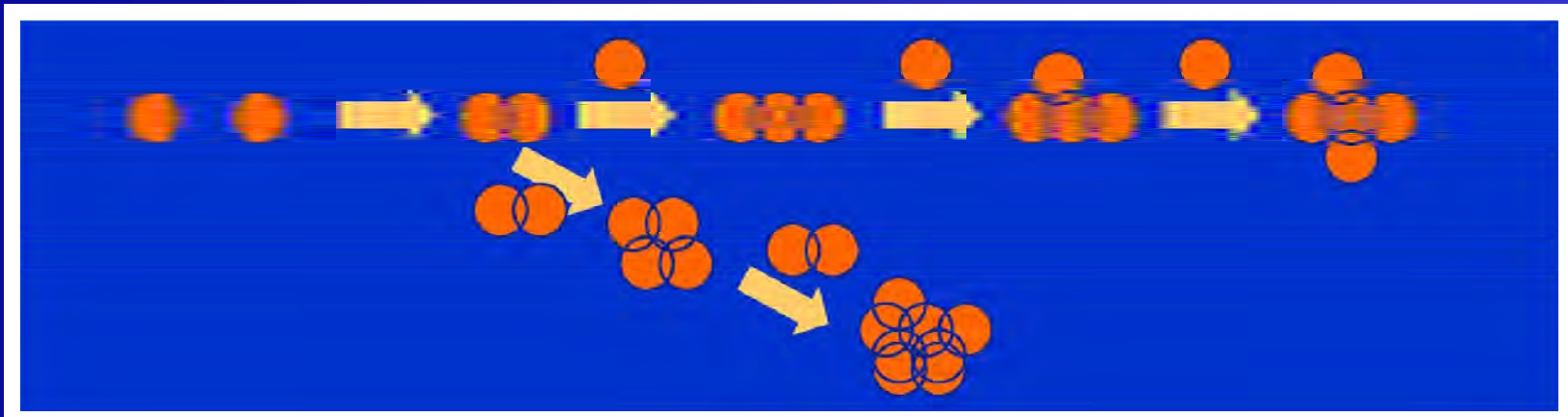
Typically performed on solids or dispersed solids



Source: Nanophase Technologies Corp.

Synthetic Strategies

- Bottom → Up
 - Nanoparticles are built up atom/molecule at a time
 - Energy is required for promoting the reactions
 - Process key – control nucleation and growth
 - Example – flame synthesis of titanium dioxide
 - Typically done in gas or liquid phases
 - Vs. Top → Down approach, usually Bottom → Up products have higher purity, better particle size/surface chemistry control



Source: Nanophase Technologies Corp.

Nanomanufacturing: typical bottom-up processes

- **Controlled nucleation and growth**
 - Aerosol and colloidal dispersions; deposition on surfaces
- **Selfassembling**
 - Natural process in living systems and biomimetics
 - Chemistry/chemical manufacturing
 - Guided by electric, magnetic, optical fields, DNA controlled ..
- **Templating:** Al and C nanotubes; by substrate; local reactors; ..
- **Engineered molecules and molecular assemblies**
 - Designed molecules as devices or for selfassembling
 - New molecular architectures by design
- **Bio methods** - Selectivity, selfassembling, synthetic biology, ..
- **Bottom-up modular nanosystems**
- **Control replicating structures (ex: cellular approach)**

M.C. Roco, 2/23/2008

Nanomanufacturing: other typical processes

- Lithography: optical, ultraviolet, electron-beam, SPM based (1-10 nm)
- Nano-machining
- Nano-manipulation of atoms, molecules, nanoparticles
- Fragmentation: mechanical milling, spark erosion, etc.
- Sintering of nano precursors
- Thermal treatment of metals, ceramics, composites
- Mixing of nanocomposites and their processing
- Fluidics
- Nanoscale robotics
- Bio-evolutionary approaches, ..

M.C. Roco, 2/23/2008

Nanoceramic Powders

- Nanoceramic powders constitute an important segment of the whole nanostructured materials.
- Constitute a third of the total new nanostructured materials.

Nanotubes

- Conductors or semiconductors
- Strong materials with good thermal conductivity

Nanocomposites

- Generally polymer based with nanosized fillers

Commercial Products

- Nanoceramics are available commercially in the form of dry powders or liquid dispersions.
- The most commercially important nanoceramic materials are simple metal oxides, silica (SiO_2), titania (TiO_2), alumina (Al_2O_3), iron oxide (Fe_3O_4 , Fe_2O_3), zinc oxide (ZnO), ceria (CeO_2) and zirconia (ZrO_2).
- Silica and iron oxide nanoparticles have a commercial history spanning half a century or more
- Of increasing importance are the mixed oxides and titanates
 - indium-tin oxide ($\text{In}_2\text{O}_3\text{-SnO}_2$ or ITO)
 - antimony-tin oxide (ATO),
 - barium titanate (BaTiO_3).
- Nanocrystalline titania, zinc oxide, ceria, ITO, and other oxides have more recently entered the marketplace.

Commercial Products Cont'd...

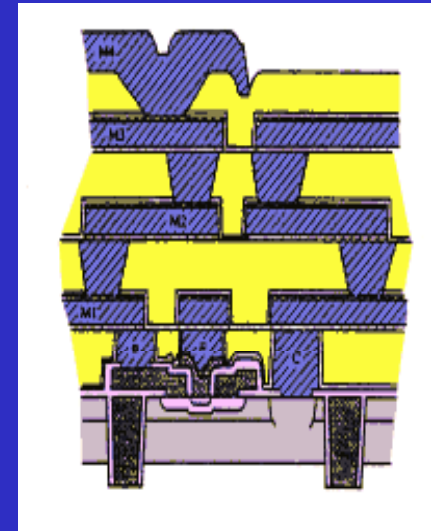
- Nonoxide ceramics, such as tungsten carbide (WC) - Under development and available in small- or pilot-scale quantities
- Except semiconducting oxides such as titania and ITO, semiconductor nanocrystals are not yet used in large-scale commercial applications; the technology to produce and utilize nanocrystalline semiconductors, often called quantum dots, is relatively new and rapidly emerging
- Two main types of nanotubes: Single Wall Nanotubes (SWNT) and Multi Wall Nanotubes (MWNT)
- SWNT – Currently emerging with large future potential
- MWNT – Used in thermoplastic nanocomposites

What's Now?

- CMP
- Magnetic fluid sealing
- Transparent functional coatings
- Magnetic recording tapes
- Hard disks and GMR heads
- Power transformer cores
- Sunscreens
- MRI contrast agents
- Biomagnetic separations...
- Sports Equipment

Chemical-Mechanical Polishing (CMP)

- Planarization of metal and dielectric layers on semiconductor wafers
- Typical abrasives used:
 - Silica
 - Alumina
 - Ceria and others



Left: Unplanarized layers.
Right: CMP-processed layers.

Source: Peter Wolters AG

Magnetic Fluid Sealing

- Dispersions of superparamagnetic iron oxide (ferrofluids)
- Current: Loudspeakers, hard disk drives, vacuum feedthroughs
- Future: MEMS/NEMS and bioapplications



Source: Ferrotec Corp.



Source: MIT

Transparent Conductive Coatings

- Indium tin oxide (ITO)
 - CRTs
 - Photographic films
 - FPD electrodes
 - Touch screens
- Films produced by:
 - Vapor deposition or
 - Nanoparticle technology



Source: 3M

Magnetic Recording Tapes

- Magnetic storage technology used for:
 - Audio cassettes
 - Videocassettes
 - Data storage tapes
 - Floppy disks
 - Hard disks, etc.
- High aspect ratio magnetic particles basis for magnetic layer of tapes
 - Iron oxide or Co-iron oxide
 - Iron and iron-cobalt



Source: S. Onodera, *MRS Bulletin*
[21, 9, 1996]

300 nm

Power Transformer Cores

- Toroidal tape-wound cores for power transformers
- Vacuumschmelze Vitroperm
- Advantages:
 - Lower weight
 - Reduced volume
 - Higher efficiency
 - Expanded temp range



Source: Vacuumschmelze

Sunscreens: Background

- UVB exposure → sunburn, carcinomas
- UVA exposure → melanoma, premature aging
- Nanoscale TiO_2 and ZnO particles provide broad-spectrum UV protection in a transparent formulation
- Opportunities in sensitive skin and baby sunscreens, also daily wear products

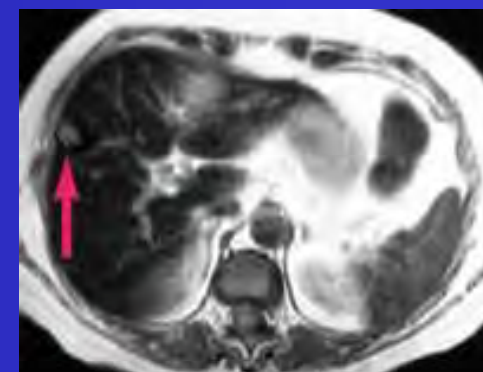


MRI Contrast Agents

Agent Type	Signal Intensity Impact	Examples
Paramagnetic	Positive	Ionic chelated gadolinium , iron or manganese, such as MnCl_2 or Gd-DTPA; oil emulsions
Superparamagnetic	Negative	Nanoscale iron oxide
Diamagnetic	Negative	(Experimental) barium sulfate suspensions; clay minerals
Perfluorochemicals	Negative	Perfluorooctylbromide

Source: BCC, Inc.

Contrast-Enhanced MRI Image



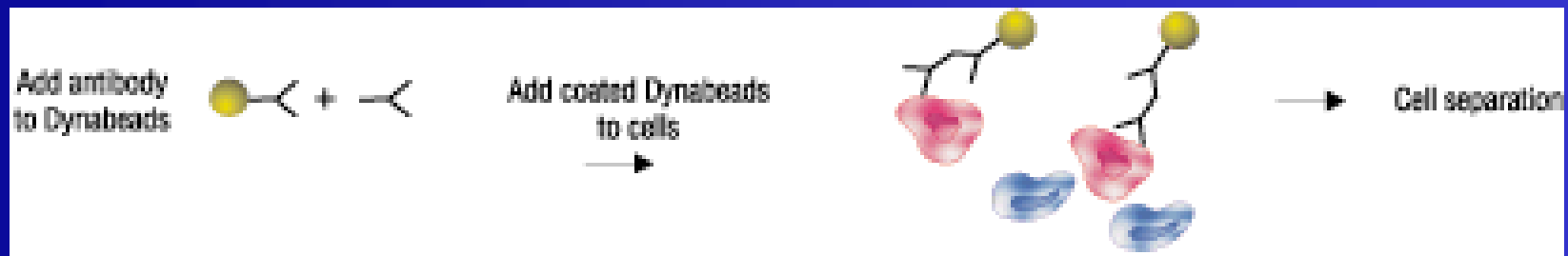
Source: Advanced Magnetics & Steven E. Harms, University of Arkansas for Medical Sciences

Gadolinium-based contrast agents

- First to gain regulatory approval
- Believed to have 60% of world market
- Usage extends beyond approved indications

Biomagnetic Separations

- Superparamagnetic iron oxide in the form of particle aggregates or composite beads
- Major applications
 - Cell sorting
 - Nucleic acid extraction/purification
 - Bacterial detection



Source: Dynal Biotech

Applications of Carbon Nanotubes for composites and displays in the market



Composites – tennis rackets and bicycles



Field Emission Displays, Samsung

Imaging and diagnostics

NanoPlex biomarker detection. These silica-coated, surface enhanced Raman scattering (SERS)-active metal nanoparticles allow robust, ultrasensitive, highly-multiplexed biomarker quantitation in any biological matrix, including whole blood



Photocatalysis

- Photocatalytic reactions can purify water, air, surfaces, and fabrics
- “Self-cleaning” or “anti-fogging” properties
- TiO₂ nanocrystals / films
- Large interest in Japan
- Potential impact in number of market segments:
 - Automotive
 - Lighting
 - Medical
 - Construction, etc.

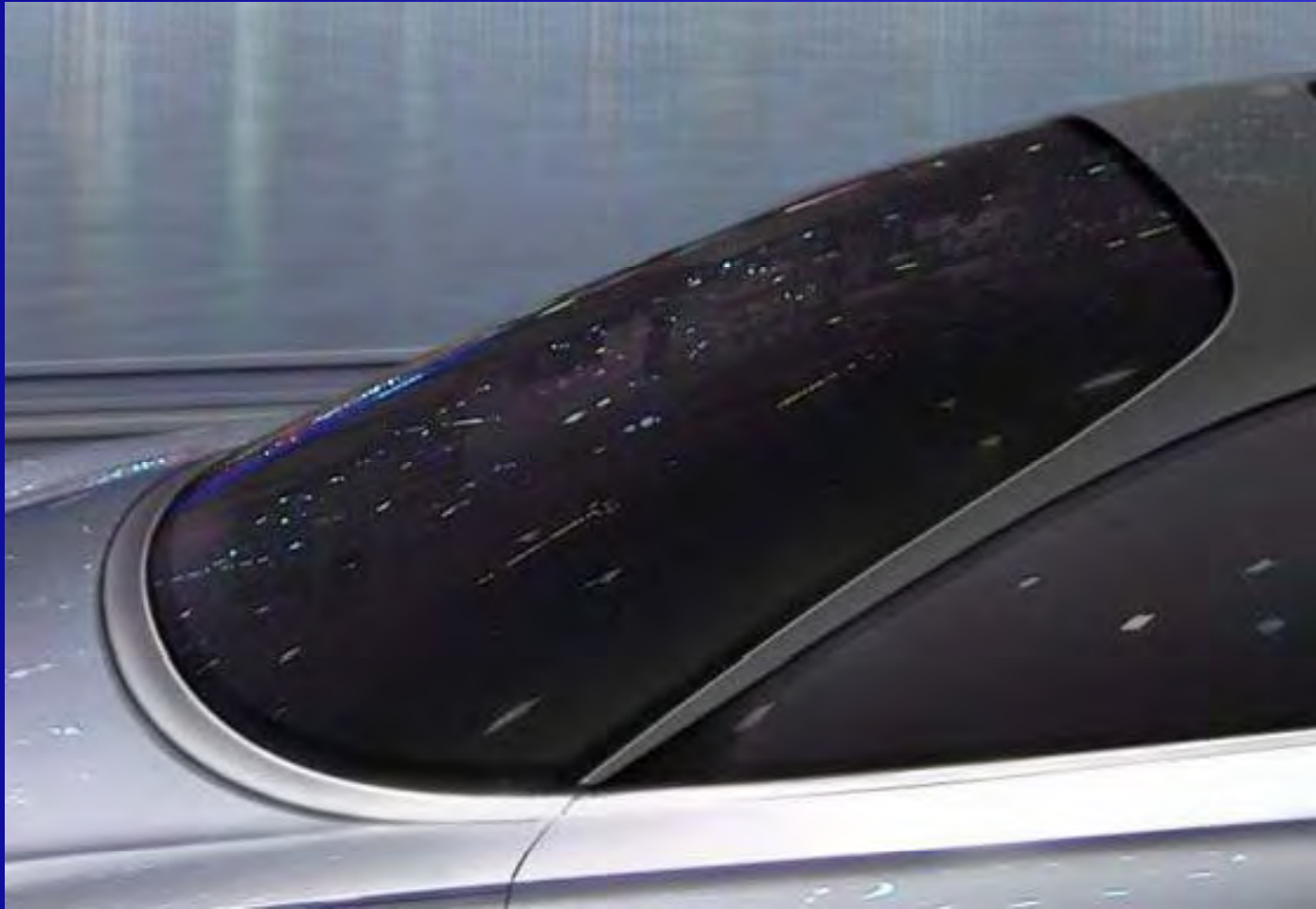


Right half of mirror only coated with photocatalytic film.

Source: TOTO, Ltd.

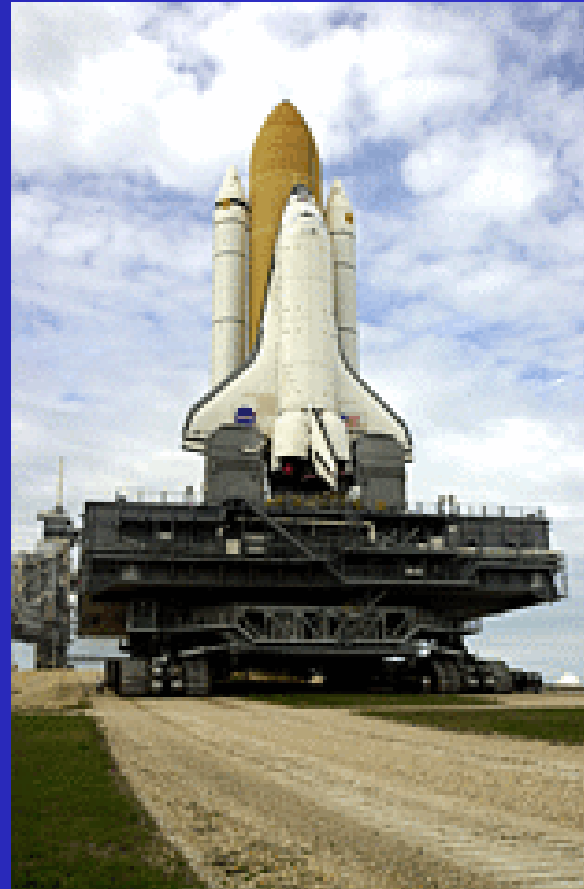
Automobile Glasses

No more windshield wipers needed



Propellants

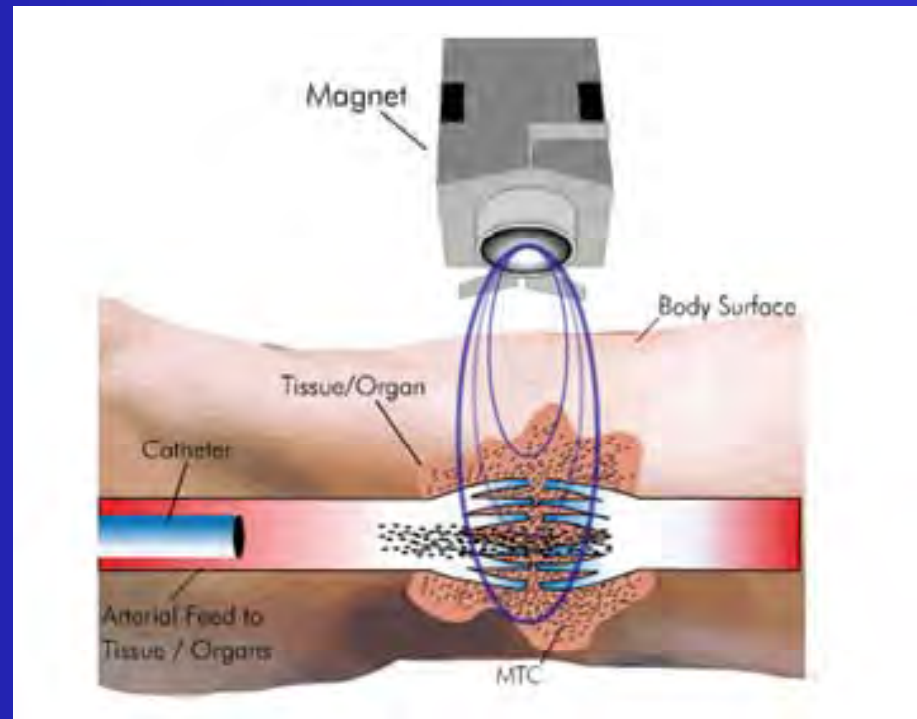
- Of the 502,126 kg of propellant used in the solid rocket boosters of the Space Shuttle, 16% (80,340 kg) is atomized aluminum powder
- Nanoscale aluminum powder higher burn rates?



Source: NASA

Drug Delivery and Disease Treatment

- Potential to revolutionize cancer treatment
- Nanocrystals: Effective agents for selective targeting and destruction of cancer cells?
 - Small particle size
 - Surface functionalization possible
 - Unique properties (magnetic, optical)



Source: FeRx, Inc.

NANOFABRICS



COURTESY DR. HONG DONG/CORNELL UNIVERSITY

A garment coated with smog-busting
palladium nanoparticles

Source: Dr. Hong Dong, Cornell University

NANO ENABLED BATTERIES

A123Systems' lithium ion batteries are enabled by proprietary nanophosphate technology.

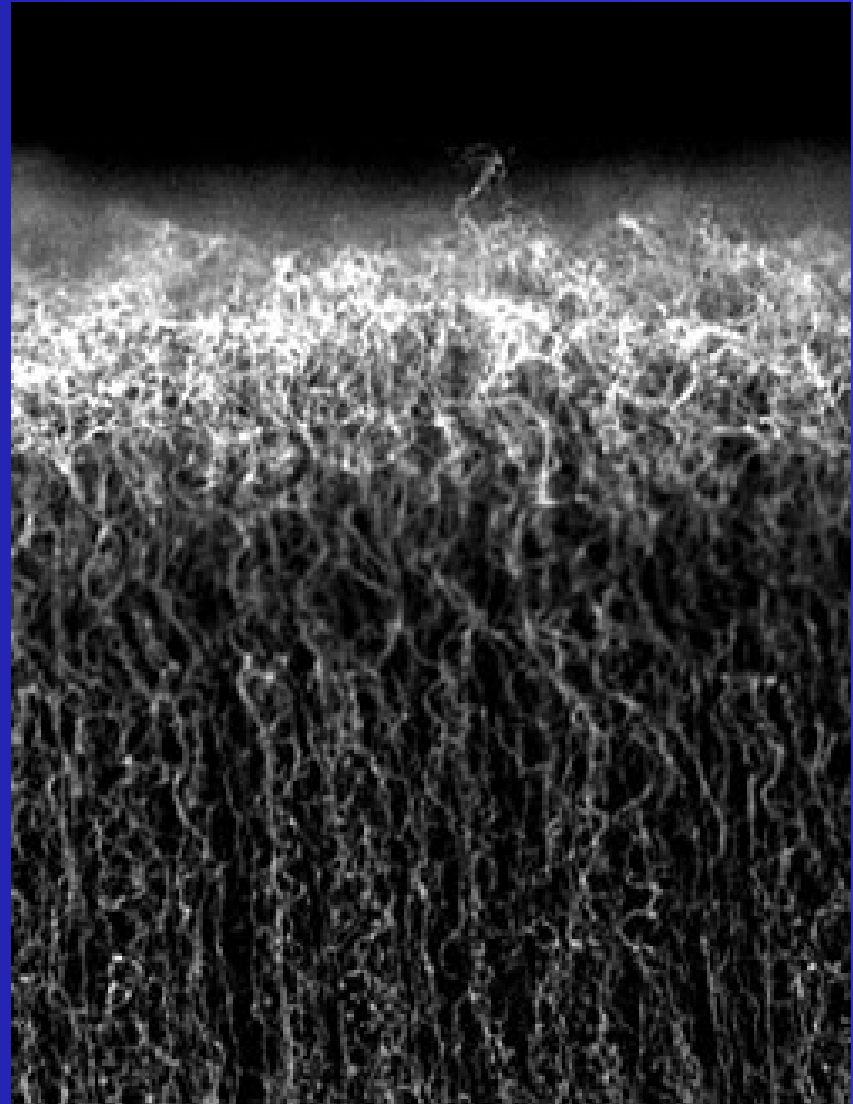


Source: A123Systems

NANO ENABLED CAPACITORS

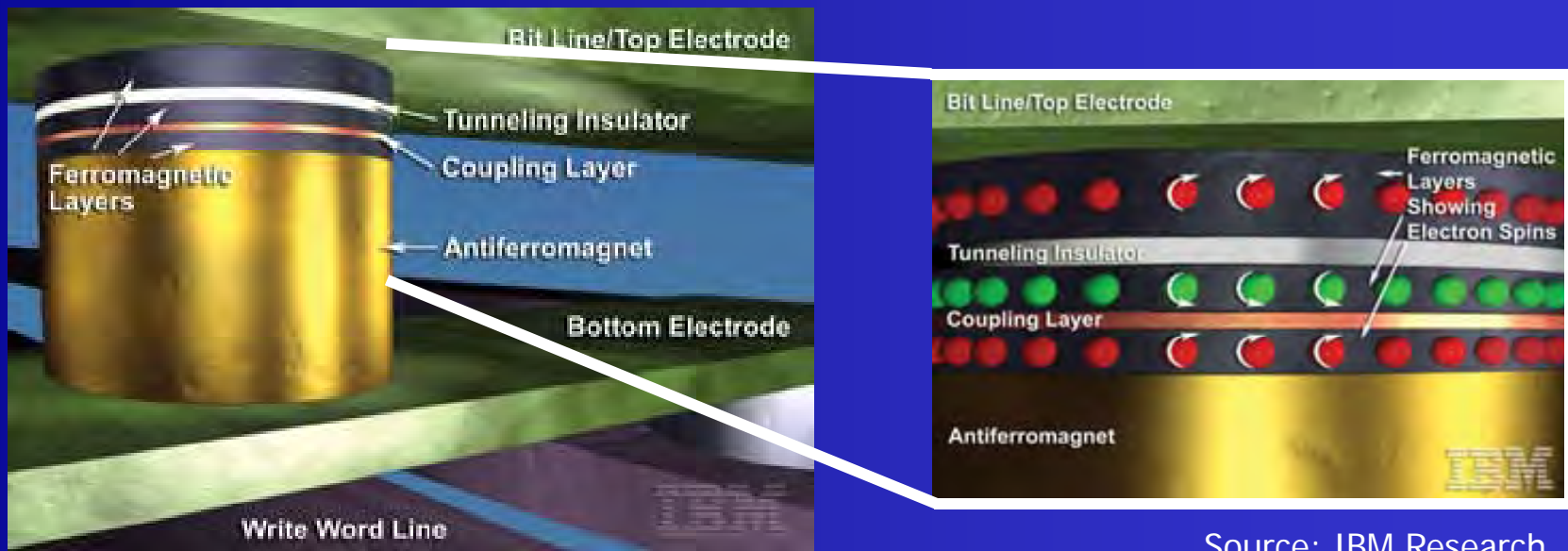
Nanotube Filaments
Ultracapacitor
Electrodes

Source: Dr. Joel Schindall, MIT



Magnetic RAM

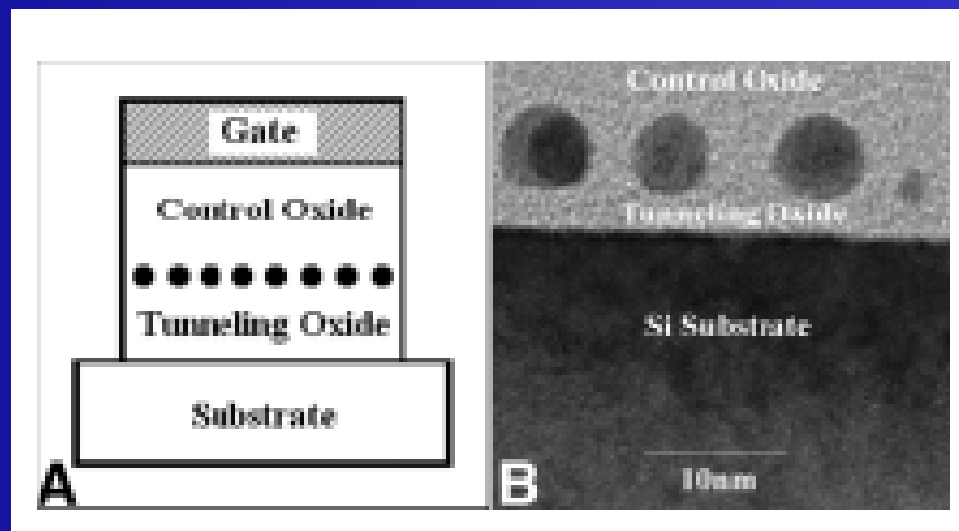
- Spintronic device; exploits spin of e- for information storage
- Touted as “universal memory”



Source: IBM Research

Silicon Nanocrystal Memory

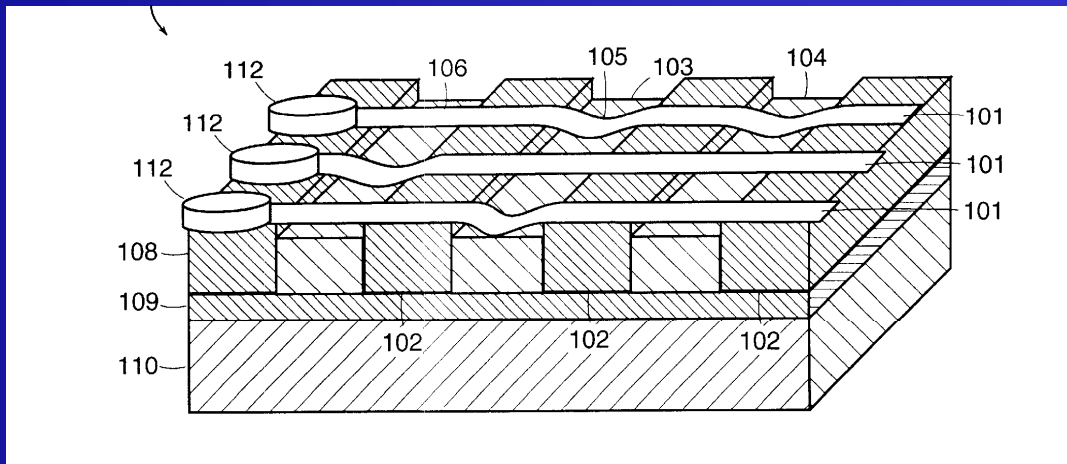
- Flash memory alternative
- Silicon nanocrystals or quantum dots replace continuous silicon film



Source: Edwin C. Kan, Cornell University

Nanotube or Nanowire Memory

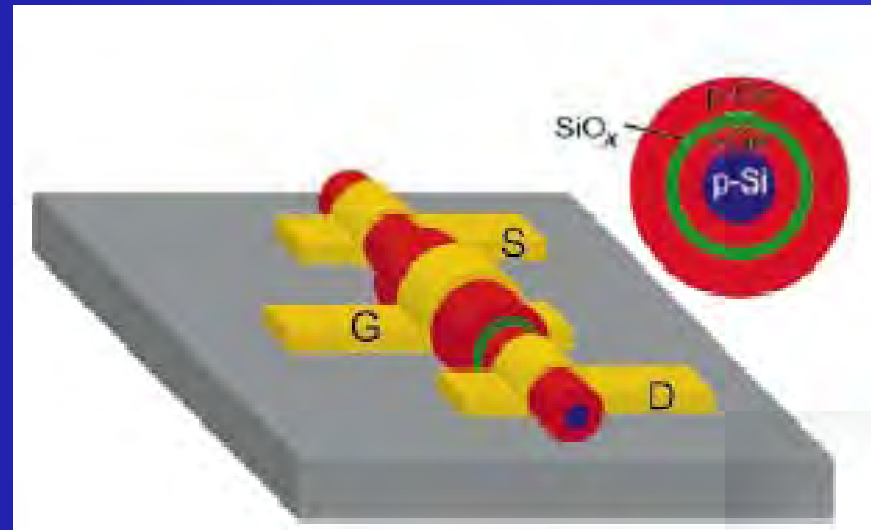
- Near term: nanotube “ribbons”
- Longer term: single nanotubes or nanowires and ultrahigh density
- Trailblazer: Nantero, Inc.



Source: U.S. Patent 6,574,130, issued to Nantero, Inc.

Logic Technologies

- Carbon nanotube FETs
- Semiconductor nanowire FETs
- Single electron transistors
- Near-term: Hybrid nano/microelectronic architecture
- Long-term: New logic architectures
 - Bottom-up fabrication
 - Ultrahigh device density
 - Fault tolerance
 - Reprogrammability
 - High speed



Source: L. Lauhon, et al., *Nature*, 420 (November, 2002) 57-61.

NANOIMPRINT LITHOGRAPHY

Full Field
Lithography at
Chip and Wafer
Level UV-NIL

Source: Suss MicroTec



GLOBAL MARKET FOR NANOMATERIALS IN SELECT SEGMENTS, 2010

	\$ MILLION	Current Growth Rate (%)
Nanomaterials (includes carbon black, polycrystalline calcium carbonate and silica fumes)	16,000	7
Nanoceramics	1,000	9
Single Wall Carbon Nanotubes (SWCNT)	180	12
Muli Wall Carbon Nanotues (SWCNT)	105	47
Nanocomposites	250	18
Carbon Nanofibers	88	10
For Electronic/Magnetic/Optoelectronic	600	16
For Biomed/Pharma/Cosmetics	400	20

GLOBAL NANOTECHNOLOGY MARKET IN SELECT SEGMENTS, 2008

CATEGORY	\$ MILLION	Current Growth Rate (%)
Nanophotonics	>8,000	>50
Nanomagnetics	6,000	20
Nanopatterning	Large	--
Nano for Life Sciences	1,200	30
Nanofiltration Membranes	100	26

Current and Potential Market for Nano-enabled Batteries, 2008-2013 (\$ Millions)

Type	2008	2013	AAGR % 2009-2013
Large Format Modules	64	960	71.8
Customized Battery Packs for Cordless Tools	100	123	4.2
Fast Charging Customized Nano Safe Battery for Laptops	5	50	58.4
Total	160	1,133	46.3

Source: iRAP, Inc. Report En-102 Nano-enabled Batteries – A
Global Industry and Market Analysis

Global Market for Fuel Cell Nanotechnology, 2008-2014 (\$ Millions)

	2008	2009	2014	AAGR % 2009-2014
Proton Exchange Membrane	800	860	1,350	9.1
Direct Methanol & Liquid Fuel Cell	270	285	355	4.5
SOFC, PAFC, MCFC	180	195	245	8.0
Hydrogen	760	850	1,140	11.4
Total Nano-Related	2,010	2,190	3,090	7.1

Source: iRAP, Inc. Report En-103 Nano-enabled Fuel Cells – A
Global Industry and Market Analysis

Global Market for Nanophotonic Devices, Through 2009 (\$ Millions)

	2003	2004	2009	AAGR % 2004-2009
Light-emitting diodes	204.8	346.1	8,759.2	90.8
Near-field optics	50.0	60.6	98.1	10.1
Solar cells	13.0	14.0	50.0	29.0
Others*	-	-	418.0	NA
Total	267.8	420.7	9,325.3	85.8

* Includes optical switches, nanophotonics ICs, holographic memory, optical amplifiers and add/drop filters

Source: Industry Sources

Global Market for Nanomagnetic Materials and Devices, Through 2009 (\$ Millions)

	2003	2004	2009	AAGR % 2004-2009
Information storage	3,400.5	4,070.0	11,480.9	23.0
Biotechnology	143.0	158.0	310.0	14.4
Industrial Products	80.6	93.0	167.1	12.4
Total	3,624.1	4,321.0	11,958.0	22.6

Source: Industry Sources

Global Demand for Semiconductor Materials, 2005 to 2014 (\$ Billions)

2005	-	28.8
2006	-	31.4
2007	-	37.6
2008	-	34.6
2009	-	25.9
2014	-	40.0

Global Market for Semiconductors, 2009 to 2010 (\$ Billions)

Source: iSupply Corp.

2009 - 230

2010 - 304

Nano-enabled Fabrication for Semiconductors,

- R&D of semiconductor equipment for 45 nm node started in 2003
- New standard now is 32 nm
- The semi fabrication is now moving toward 22 nm

- Each reduction results in more powerful microprocessors, memory chips and Si based solar collectors.

- Close to 40% semiconductors are now produced under the nano-fabrication platform (65, 45 and 32 nm node and the trend is further down to 22 nm node)

Materials Demand and Semiconductor Value Under Nano Platform, 2008 to 2014 (\$ Billions)

		Materials	Semi Values
2008	-	11.4	
2009	-	10.7	~70
2010	-	11.7	~90
2014	-	20.6	

Global Market for Nano-enabled Packaging in the Food/Beverage and Pharma Industry , 2014 (\$ Billions)

	2008	2009	2014	CAGR % 2009-2014
Food/Beverage Packaging	4.13	4.21	7.30	11.65
Pharma Packaging	3.60	3.78	8.10	16.48

Source: iRAP, Inc.

Conclusions

- **Nanoscale materials engineering will have an increasingly important impact on a number of sectors, including biotechnology, electronics, information technology, energy, aerospace and industrial products**
- **Nano-sized ceramic powder market is likely to grow with a healthy growth rate of about 10% per year in the next five years**
- **SWNT are likely to see some exciting applications such as microscope probe tips (already commercially available), field emission devices (one device, an X-ray fluorometer which makes use of a cold cathode nanotube is commercially available) and some membrane applications. MWNT filled polymers are successful commercial products in automotive applications.**
- **Nanocomposites have found niche applications such as automotive (under the hood and exterior) and beverage packaging.**

Conclusions Cont'd...

- More companies will enter the nanomaterials market. At the same time, there will be increasing number of business relations such as technology licensing and joint marketing to achieve faster commercialization of the new products
- The research and development funding for nanotechnology and nanomaterials will continue to increase in this decade.
- Numerous technological and market hurdles to commercialization exist. Success can be achieved only with a keen understanding of the basic science as applied to actual production requirements and market needs.

Nanotechnology 2011 Conference

**NANOMATERIALS AND NANOCHEMISTRY,
NANO-ENABLED ENERGY SYSTEMS,
NANOMEDICINE AND NANO-BIO
CONVERGENCE- Emphasizing Emerging Science and
Technologies, Applications, Commercialization and
Business Opportunities**

Organized by *iRAP* and American Institute of Chemical Engineers

Javits Convention Center, New York, NY

November 1-3, 20011



iRAP Reports

- **Nanomaterials, Nanoceramics, Nanocarbon Products**
- **Nano-enabled Fuel Cells**
- **Nanolithography Equipment**
- **Nano-enabled Batteries**
- **Nano-enabled Packaging for Food & Beverages and Pharma**
- **Ultracapacitors and Thin Film Batteries**
- **Lithium Ion Batteries**
- **Piezoelectric Operated Motors and Actuators**
- **MEMS Microphones and Oscillators**
- **Micro Fuel Cells for Flexible Handheld Devices**
- **Electroactive Polymer Devices**
- **Piezoelectric Crystal, Ceramic and Polymer Devices**

THANK YOU

Dr. Thomas Abraham

President

Innovative Research and Products (*iRAP*)

P.O. Box 16760, Stamford, CT 06905, USA

Tel: 203-569-7909

E-mail: tabraham@innoresearch.net

Web: www.innoresearch.net