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

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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

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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-)

1st: Passive nanostructures
Ex: coatings, nanoparticles, nanostructured metals, polymers, ceramics

2nd: Active nanostructures
Ex: 3D transistors, amplifiers, targeted drugs, actuators, adaptive structures

3rd: Systems of nanosystems
Ex: guided assembling; 3D networking and new hierarchical architectures, robotics, evolutionary

4th: Molecular nanosystems
Ex: molecular devices ‘by design’, atomic design, emerging functions

5th: Converging technologies
Ex: nano-bio-info from nanoscale, cognitive technologies; large complex systems from nanoscale


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Context – Nanotechnology in the World
National government investments 1997-2006 (est. NSF)

Seed funding (1991 - )
NNI Preparation (vision / benchmark)
1st Strategic Plan (passive nanostructures)

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

2nd Strategic Plan (active ns. & systems)

J. Nanoparticle Research, 7(6), 2005, MC Roco
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<table>
<thead>
<tr>
<th>Year</th>
<th>-</th>
<th>Budget (Millions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006</td>
<td>-</td>
<td>$1,351</td>
</tr>
<tr>
<td>2007</td>
<td>-</td>
<td>$1,425</td>
</tr>
<tr>
<td>2008</td>
<td>-</td>
<td>$1,554</td>
</tr>
<tr>
<td>2009</td>
<td>-</td>
<td>$1,650</td>
</tr>
<tr>
<td>2010</td>
<td>-</td>
<td>$1,913</td>
</tr>
<tr>
<td>2011</td>
<td>-</td>
<td>$1,805 (Estimated)</td>
</tr>
<tr>
<td>2012</td>
<td>-</td>
<td>$2,129 (Proposed)</td>
</tr>
</tbody>
</table>
Growing nanotechnology R&D investment - $12.6 billion in 2006

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
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, ..
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$_2$O$_3$), iron oxide (Fe$_3$O$_4$, Fe$_2$O$_3$), zinc oxide (ZnO), ceria (CeO$_2$) and zircona (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 (In$_2$O$_3$-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.
• 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

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Transparent Conductive Coatings

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

Source: 3M

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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

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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

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# MRI Contrast Agents

<table>
<thead>
<tr>
<th>Agent Type</th>
<th>Signal Intensity Impact</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Paramagnetic</strong></td>
<td>Positive</td>
<td>Ionic chelated gadolinium, iron or manganese, such as MnCl₂ or Gd-DTPA; oil emulsions</td>
</tr>
<tr>
<td><strong>Superparamagnetic</strong></td>
<td>Negative</td>
<td>Nanoscale iron oxide</td>
</tr>
<tr>
<td><strong>Diamagnetic</strong></td>
<td>Negative</td>
<td>(Experimental) barium sulfate suspensions; clay minerals</td>
</tr>
<tr>
<td><strong>Perfluorochemicals</strong></td>
<td>Negative</td>
<td>Perfluorocetyl bromide</td>
</tr>
</tbody>
</table>

**Gadolinium-based contrast agents**
- First to gain regulatory approval
- Believed to have 60% of world market
- Usage extends beyond approved indications

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

*Source: BCC, Inc.*
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
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?
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.
A garment coated with smog-busting palladium nanoparticles
Source: Dr. Hong Dong, Cornell University
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”
Silicon Nanocrystal Memory

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

Source: Edwin C. Kan, Cornell University

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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

NANOIMPRINT LITHOGRAPHY

Full Field Lithography at Chip and Wafer Level UV-NIL

Source: Suss MicroTec
## GLOBAL MARKET FOR NANOMATERIALS IN SELECT SEGMENTS, 2010

<table>
<thead>
<tr>
<th>Segment</th>
<th>$ MILLION</th>
<th>Current Growth Rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanomaterials (includes carbon black, polycrystalline calcium carbonate and silica fumes)</td>
<td>16,000</td>
<td>7</td>
</tr>
<tr>
<td>Nanoceramics</td>
<td>1,000</td>
<td>9</td>
</tr>
<tr>
<td>Single Wall Carbon Nanotubes (SWCNT)</td>
<td>180</td>
<td>12</td>
</tr>
<tr>
<td>Muli Wall Carbon Nanotues (SWCNT)</td>
<td>105</td>
<td>47</td>
</tr>
<tr>
<td>Nanocomposites</td>
<td>250</td>
<td>18</td>
</tr>
<tr>
<td>Carbon Nanofibers</td>
<td>88</td>
<td>10</td>
</tr>
<tr>
<td>For Electronic/Magnetic/Optoelectronic</td>
<td>600</td>
<td>16</td>
</tr>
<tr>
<td>For Biomed/Pharma/Cosmetics</td>
<td>400</td>
<td>20</td>
</tr>
</tbody>
</table>
## GLOBAL NANO TECHNOLOGY MARKET IN SELECT SEGMENTS, 2008

<table>
<thead>
<tr>
<th>CATEGORY</th>
<th>$ MILLION</th>
<th>Current Growth Rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanophotonics</td>
<td>&gt;8,000</td>
<td>&gt;50</td>
</tr>
<tr>
<td>Nanomagnetics</td>
<td>6,000</td>
<td>20</td>
</tr>
<tr>
<td>Nanopatterning</td>
<td>Large</td>
<td>--</td>
</tr>
<tr>
<td>Nano for Life Sciences</td>
<td>1,200</td>
<td>30</td>
</tr>
<tr>
<td>Nanofiltration Membranes</td>
<td>100</td>
<td>26</td>
</tr>
</tbody>
</table>

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### Current and Potential Market for Nano-enabled Batteries, 2008-2013

($ Millions)

<table>
<thead>
<tr>
<th>Type</th>
<th>2008</th>
<th>2013</th>
<th>AAGR % 2009-2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large Format Modules</td>
<td>64</td>
<td>960</td>
<td>71.8</td>
</tr>
<tr>
<td>Customized Battery Packs for Cordless Tools</td>
<td>100</td>
<td>123</td>
<td>4.2</td>
</tr>
<tr>
<td>Fast Charging Customized Nano Safe Battery for Laptops</td>
<td>5</td>
<td>50</td>
<td>58.4</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>160</strong></td>
<td><strong>1,133</strong></td>
<td><strong>46.3</strong></td>
</tr>
</tbody>
</table>


($ Millions)

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

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

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Light-emitting diodes</td>
<td>204.8</td>
<td>346.1</td>
<td>8,759.2</td>
<td>90.8</td>
</tr>
<tr>
<td>Near-field optics</td>
<td>50.0</td>
<td>60.6</td>
<td>98.1</td>
<td>10.1</td>
</tr>
<tr>
<td>Solar cells</td>
<td>13.0</td>
<td>14.0</td>
<td>50.0</td>
<td>29.0</td>
</tr>
<tr>
<td>Others*</td>
<td>-</td>
<td>-</td>
<td>418.0</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>267.8</td>
<td>420.7</td>
<td>9,325.3</td>
<td>85.8</td>
</tr>
</tbody>
</table>

* 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)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Information storage</td>
<td>3,400.5</td>
<td>4,070.0</td>
<td>11,480.9</td>
<td>23.0</td>
</tr>
<tr>
<td>Biotechnology</td>
<td>143.0</td>
<td>158.0</td>
<td>310.0</td>
<td>14.4</td>
</tr>
<tr>
<td>Industrial Products</td>
<td>80.6</td>
<td>93.0</td>
<td>167.1</td>
<td>12.4</td>
</tr>
<tr>
<td>Total</td>
<td>3,624.1</td>
<td>4,321.0</td>
<td>11,958.0</td>
<td>22.6</td>
</tr>
</tbody>
</table>

Source: Industry Sources
## Global Demand for Semiconductor Materials, 2005 to 2014 ($ Billions)

<table>
<thead>
<tr>
<th>Year</th>
<th>Demand</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005</td>
<td>28.8</td>
</tr>
<tr>
<td>2006</td>
<td>31.4</td>
</tr>
<tr>
<td>2007</td>
<td>37.6</td>
</tr>
<tr>
<td>2008</td>
<td>34.6</td>
</tr>
<tr>
<td>2009</td>
<td>25.9</td>
</tr>
<tr>
<td>2014</td>
<td>40.0</td>
</tr>
</tbody>
</table>
## Global Market for Semiconductors, 2009 to 2010 ($ Billions)

Source: iSupply Corp.

<table>
<thead>
<tr>
<th>Year</th>
<th>Value</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>2009</td>
<td>230</td>
<td>-</td>
</tr>
<tr>
<td>2010</td>
<td>304</td>
<td>-</td>
</tr>
</tbody>
</table>
Nano-enabled Fabrication for Semiconductors,

- R&D of semiconductor equipment for 45 nm mode 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)

<table>
<thead>
<tr>
<th>Year</th>
<th>Materials</th>
<th>Semi Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>2008</td>
<td>-</td>
<td>11.4</td>
</tr>
<tr>
<td>2009</td>
<td>-</td>
<td>10.7 ~70</td>
</tr>
<tr>
<td>2010</td>
<td>-</td>
<td>11.7 ~90</td>
</tr>
<tr>
<td>2014</td>
<td>-</td>
<td>20.6</td>
</tr>
</tbody>
</table>
### Global Market for Nano-enabled Packaging in the Food/Beverage and Pharma Industry, 2014 ($ Billions)

<table>
<thead>
<tr>
<th></th>
<th>2008</th>
<th>2009</th>
<th>2014</th>
<th>CAGR % 2009-2014</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food/Beverage Packaging</td>
<td>4.13</td>
<td>4.21</td>
<td>7.30</td>
<td>11.65</td>
</tr>
<tr>
<td>Pharma Packaging</td>
<td>3.60</td>
<td>3.78</td>
<td>8.10</td>
<td>16.48</td>
</tr>
</tbody>
</table>

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 NANO CHEMISTRY, 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, 2011

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- 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

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THANK YOU

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