

# Nano Manufacturing at NSF within CMMI

**Cerry Klein**

Program Director  
Manufacturing Enterprise Systems



# Nano in CMMI

The Advanced Manufacturing Cluster supports fundamental research leading to transformative advances in manufacturing and building technologies across size scales from nanometers to kilometers, with emphases on efficiency, economy, and minimal environmental footprint. Research is supported to develop predictive and real-time models, novel experimental methods for manufacturing and assembly of macro, micro, and nanoscale devices and systems, and advanced sensing and control techniques for manufacturing processes.

## Programs:

- **Manufacturing and Construction Machines and Equipment (MCME)**
- **Materials Processing and Manufacturing (MPM)**
- **Manufacturing Enterprise Systems (MES)**
- **Nanomanufacturing (NM)**

# Disclaimer

I do not work in nano. I am here  
to learn from you



# Manufacturing and Construction Machines and Equipment

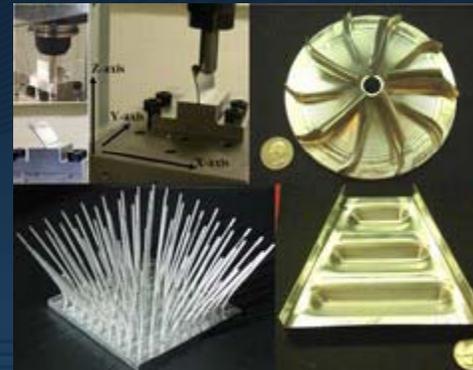
George Hazelrigg, Program Director

## Mission

The MCME program supports research on fundamental issues that relate to the advancement of manufacturing and construction machines and equipment and their use

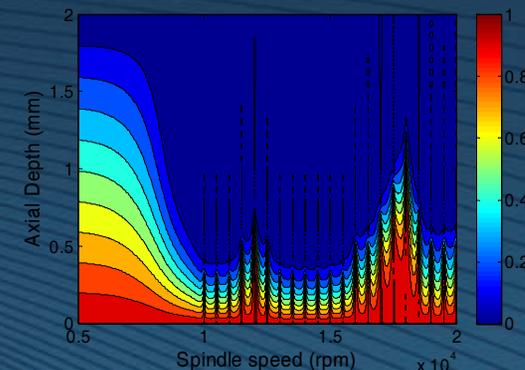
### Traditional Research Areas

- Material removal
- Material addition
- Sensing and control
- Planning and optimization
- Metrology/QC
- Manufacturing machine design
- Construction machine design



### Emerging Research Thrusts

- Energy manufacturing—the conversion of sunlight, air and water into energy products



# NanoManufacturing

## Shaochen Chen, Program Director

### Mission

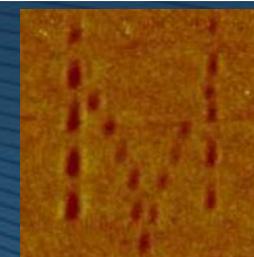
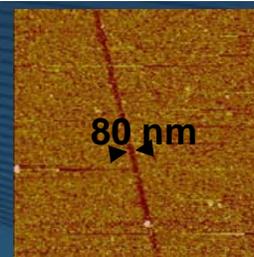
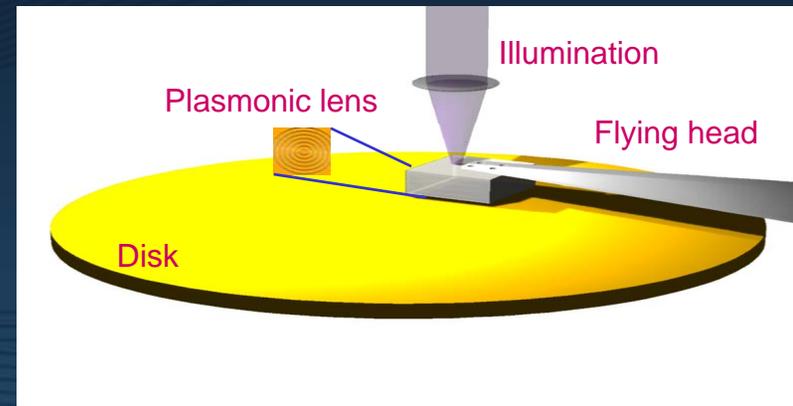
To support research and education on manufacturing at the nanoscale, and the transfer of research results in nanoscience and nanotechnology to industrial applications. The Program emphasizes a systems approach to scale-up of nanotechnology for high rate production, reliability, robustness, yield and cost and promotes integration of nanostructures to functional micro devices and meso/microscale systems.

#### Traditional Research Areas

- Nanomanufacturing processes
- Nanomanufacturing systems
- Nanomanufactured devices

#### Emerging Research Thrusts

- NanoManufacturing for energy
  - > Energy production
  - > Energy efficiency
- NanoManufacturing for human health
  - > Bionanomanufacturing
  - > Nano-enabled drug delivery



# NanoManufacturing

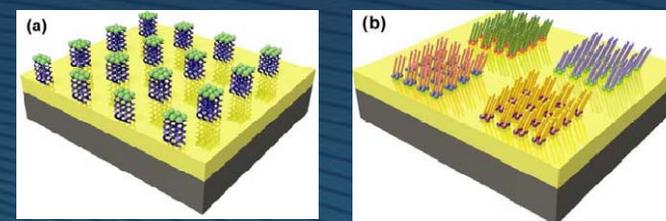
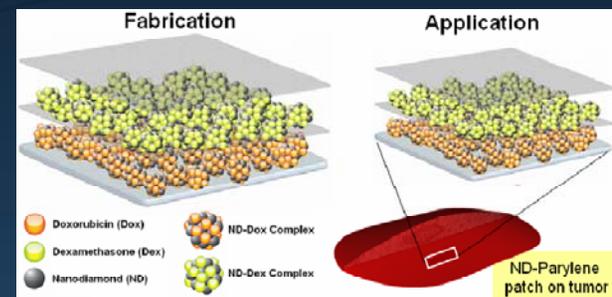
Fiscal Year	Program Budget	Addition Funds Received	No. of Proposals Received	No. of Awards	No. of SGER Awards	No. of Workshop Awards
2006	\$6,772,700	\$4,435,865	171	25	3	4
2007	\$6,786,579	\$1,682,951	200	26	2	3
2008	\$7,939,511	\$3,855,540	141	25	5	1

## Recent Advances Funded by the Program:

0846323, Dean Ho, CAREER: Scalable Fabrication of Nanodiamond Patch Platforms for Sustained Drug Release, \$425,367.

0826219, Teri Odom, Large-area Chemical, Biological, and Materials NanoManufacturing, \$350,000

0609115, Ray Baughman, NIRT: Hierarchical Nanomanufacturing of Carbon Nanotube Sheets and Yarns and Their Applications for Active Nano-Materials Systems, \$1,000,000.



# Manufacturing Enterprise Systems

Cerry M. Klein, Program Director

## Mission

To transform manufacturing enterprises through the discovery of fundamental knowledge and science and by its application to make manufacturing enterprises more global, information intensive, efficient, reactive, and environmentally friendly

### Traditional Research Areas

- Production, Material Handling, Scheduling
- Supply Chains
- Quality, Reliability, Process Control



### Emerging Research Thrusts

- Sustainability (Green Manufacturing)
- Nano-manufacturing
  - > Quality and Reliability Issues
  - > Scale up issues
  - > Multi-scale
- Energy Systems



# Manufacturing Enterprise Systems

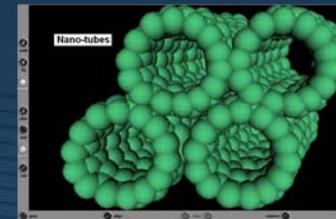
Fiscal Year	Program Budget	Addition Funds Received	Secondary Cost Share	No. of Proposals Received	No. of Awards <sup>3</sup>	No. of SGER Awards	No. of Workshop Awards
2006	\$5,652,502	\$192,000	\$212,000	134	21	3	4
2007	\$5,443,671	\$330,175	\$804,452	134	22	1	0
2008	\$4,775,426	\$122,900	\$394,484	124	18	1	1
ARRA	\$1,420,000				6	1	

## Recent Advances Funded by the Program:

0926084 Shiyu Zhou *Statistical Analysis and Control of Ultrasonic-based Aluminum Nano-composite Fabrication Processes*



0728100 Qiang Huang *In Situ Nanomanufacturing Process Control through Multiscale Nanostructure Growth Modeling.*



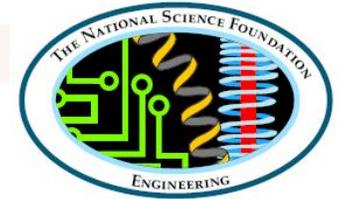
0926379 Yue Kuo and Yao Yuan *Collaborative Research: Nonparametric Bayesian Modeling of Reliability of Nanoelectronics*



# Future?

- How do we scale up?
- What are the fundamental issues in nano manufacturing related to quality, reliability, and yield management?
- What are the fundamental issues in terms of nano process control?
- What currently is preventing the commercialization of nano?





# **Interdisciplinary Research (IDR) in Nanomanufacturing**

**NSF Workshop on Sensing and Prognostics for  
Scalability of Nanomanufacturing**

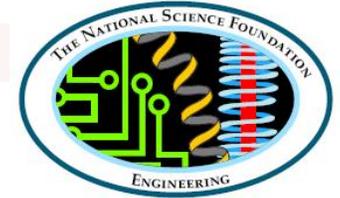
**Northeastern University**

**Boston, MA**

**November 3, 2009**

**Bruce M. Kramer**

**Director, Interdisciplinary and Cross-Directorate Programs  
Division of Civil, Mechanical and Manufacturing Innovation**

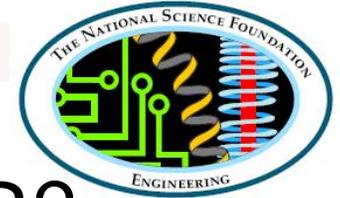


# IDR Mission

**The Directorate for Engineering (ENG) encourages submission of transformative, interdisciplinary research proposals to its programs and will be piloting a new review procedure designed to ensure that such proposals are properly evaluated.**

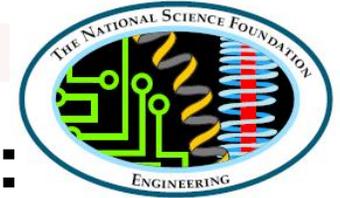
## **Definition of Interdisciplinary Research**

**“Interdisciplinary research (IDR) is a mode of research by teams or individuals that integrates information, data, techniques, tools, perspectives, concepts, and/or theories from two or more disciplines or bodies of specialized knowledge to advance fundamental understanding or to solve problems whose solutions are beyond the scope of a single discipline or area of research practice.” - National Academies**



## Should I submit my proposal to IDR?

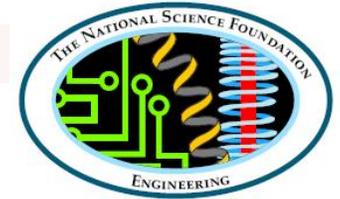
- **Most nanomanufacturing proposals meet the National Academies' definition of interdisciplinary**
- **Probably not the best decision criterion to use**
- **Suggest you select the review procedure that obtains the best possible review for your proposed work (final decision is NSF's)**
  - **Will the reviewers in a disciplinary program understand the issues? – if so, you'll get an in-depth, expert review there**
  - **Will adequate review expertise be available if you designate a secondary disciplinary program for review?**
  - **Remaining proposals may be strong candidates for the IDR process**
  - **The IDR Panel will comprise ~20 reviewers covering all fields of engineering, so in-depth expertise may not be available. Proposals must be written to this audience.**



## 2009 IDR Submission Requirements:

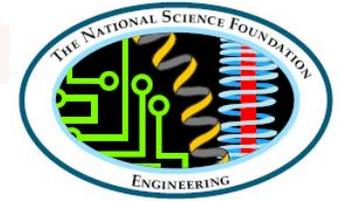
[http://www.nsf.gov/funding/pgm\\_summ.jsp?pims\\_id=503439&org=ENG&from=home](http://www.nsf.gov/funding/pgm_summ.jsp?pims_id=503439&org=ENG&from=home)

- Submission Deadline is 5:00 PM local time on December 7, 2009
- The primary Division must be in the Engineering Directorate.
- Proposals must be submitted to PD 09-7951 and Program Element 7951 in one of the three following Divisions within ENG:
  - 1) Chemical, Bioengineering, Environmental, and Transport Systems (CBET)
  - 2) Civil, Mechanical and Manufacturing Innovation (CMMI)
  - 3) Electrical, Communications and Cyber Systems (ECCS)
- Typically 2-4 investigators
- Proposal title must start with “IDR:”
- Must explicitly address the interdisciplinary nature of the proposed research in a separate paragraph in the Project Summary
- IDR should be prepared so that reviewers from different fields can appreciate the intellectual merit, transformative nature, and broader impact of the interdisciplinary research proposed.



# IDR Award Duration and Size

- All awards are typically for a duration of up to 3 years, but may be longer if circumstances warrant and are well-justified.
- Typical award size of \$400,000 to \$600,000, cumulative total.
- Awards up to \$1,000,000 will be considered, if well-justified



# IDR Proposal Review

Evaluated using NSF's two merit review criteria:

- What is the intellectual merit of the proposed activity?
- What are the broader impacts of the proposed activity?

Additional IDR review criterion:

- Degree of **interdisciplinary**.



Center for Nanoscale  
Chemical-Electrical-Mechanical  
Manufacturing Systems



# Challenges and a Few Solutions to Scalable and Robust Nanomanufacturing

Placid M. Ferreira, UIUC  
November 2009



an NSF-sponsored center for nanoscale science and engineering

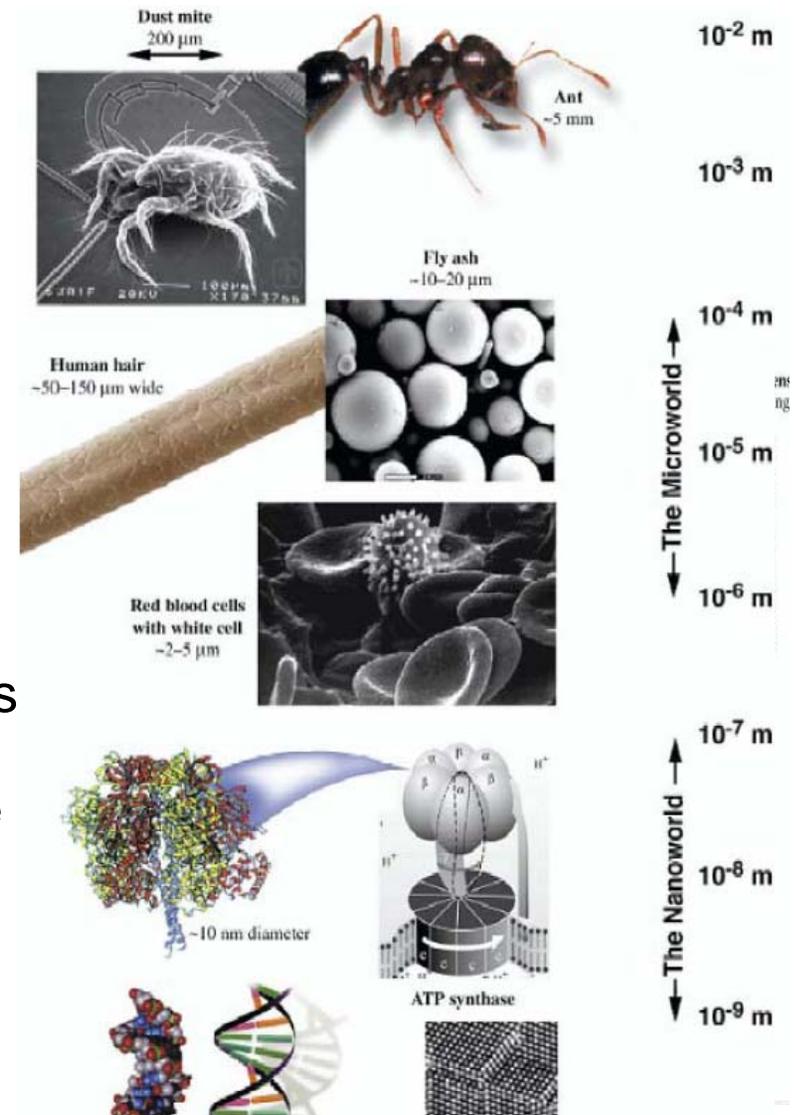


# Motivation



## ■ Why robust & scalable nanomanufacturing is difficult?

- Results must bridge 9 orders of magnitude in dimensional scales.
- Exploiting nanoscale phenomena implicitly implies taking advantage of nonlinearities. These are highly dimension dependent.
- Energy levels for sensing and processing are of the same order of magnitude.
- Useful systems will typically have a large number of structures and devices
- Environmental variations are often orders-of-magnitude higher than those permitted for processes and tools
- At the nanoscale, disturbance of many origins (mechanical, chemical, electromagnetic, etc. have roughly the same order-of-magnitude influence



\*Scaled figures taken from a presentation by R. Seigel



# Challenges



- Process Technology
- Manufacturing Tools
- Nanoscale Sensing
- Nanoscale Calibration
- Integration



# Process Technology



- **Context:** NanoManufacturing is currently practiced (in the semiconductor industry), but the efficiency of dimensional scaling is obtained by
  - Very small and tightly controlled material sets
  - Few, but repeated processes and geometry
  - Functional systems that are of  $10^{-3}$  m size scales
- **Need:** Process technology that is capable of
  - Working a large diversity of materials typically not associated with semi-conductor processing
  - Operating in ambient conditions in a continuous mode instead of UHV
  - Area coverage that may span several meters



# Process Technology



- In other words, we need processes like **Stamping, Imprinting, Embossing, Printing, Ink-jet Printing, Direct-writing** that are
  - Capable of parallel operations and are therefore fast and capable of covering large areas
  - Operate in ambient condition
  - Operate in continuous or semi-continuous modes and are amenable to roll-to-roll type process configurations
  - Versatile, with possibility of processing different material sets

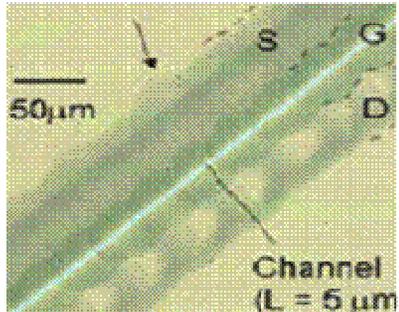


# Process Technologies (Examples)

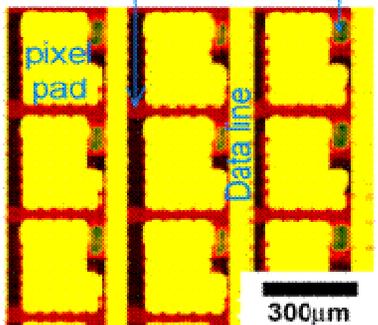


## Ink Jet (E-jet) Printing Applications

***For Printed Electronics,***



OTFT (single device)



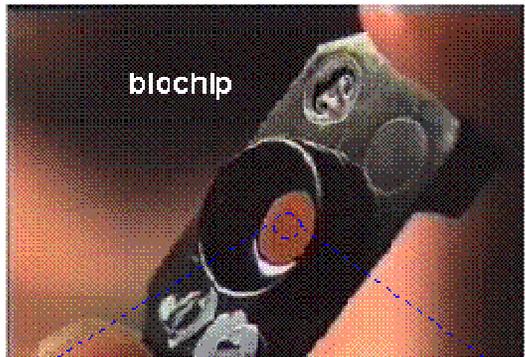
Active matrix TFT backplane



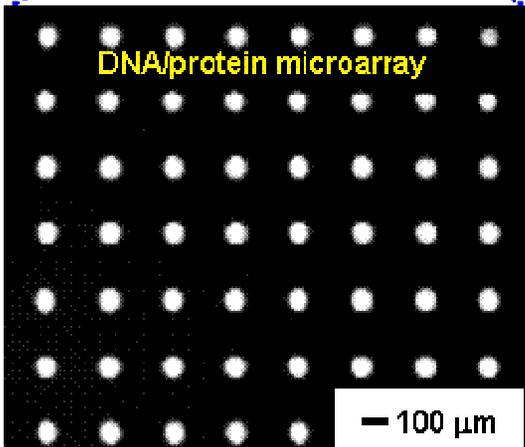
Color filter printing  
for 8G large LCD  
(Sharp, 2006)

*Science*, 290, 2123 (2000), *APL*, 85, 3304 (2004)

***For Biotechnology,***



biochip

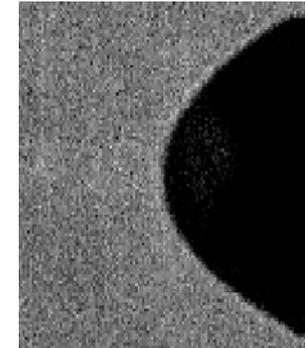
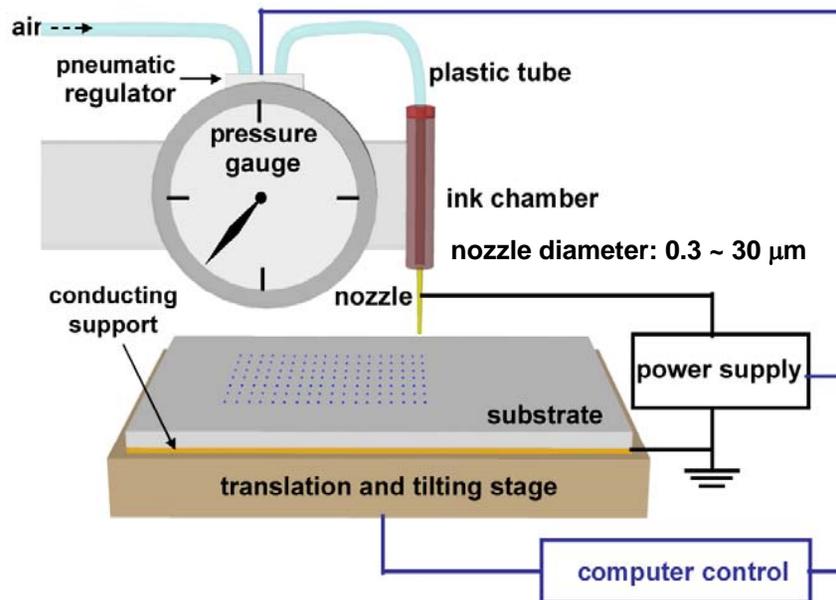


DNA/protein microarray

*Nature Biotech.*, 18, 438 (2000)



# High Resolution E-Jet Printing



- Jet diameter much smaller than nozzle diameter.
- Nozzles with very small diameters can be used.
- ⇒ advantageous for high resolution printing



# Materials Versatility & Resolution of E-jet



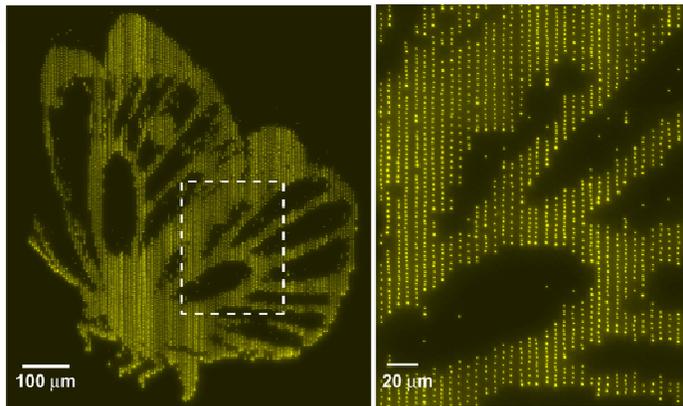
## Diversity of materials:

conducting / dielectric  
polymers, silver nanoparticles,  
Si quantum dots, CNTs,  
biomaterials (DNA), etc

(viscosity: 1 ~ 1,000 cP ,  
conductivity:  $10^{-6}$  ~  $10^{-1}$  S/m )

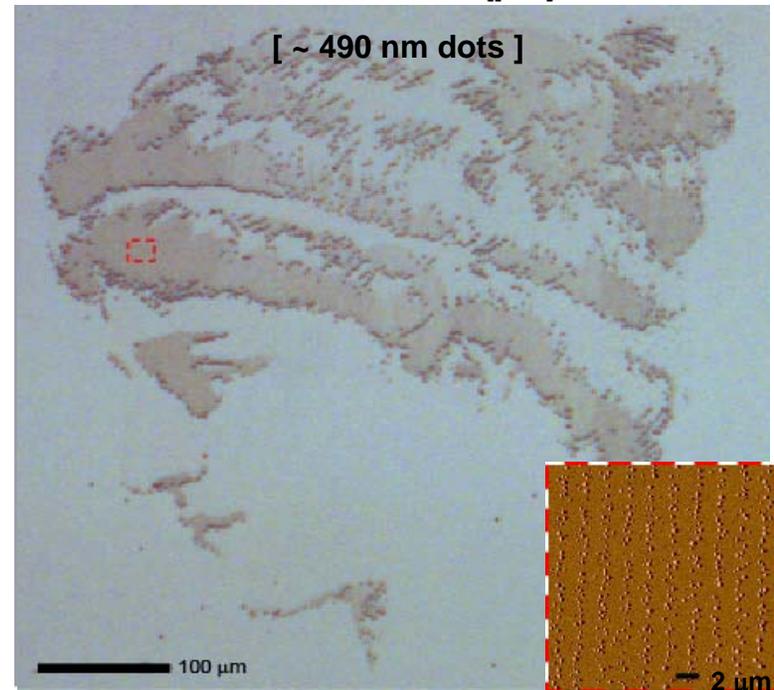
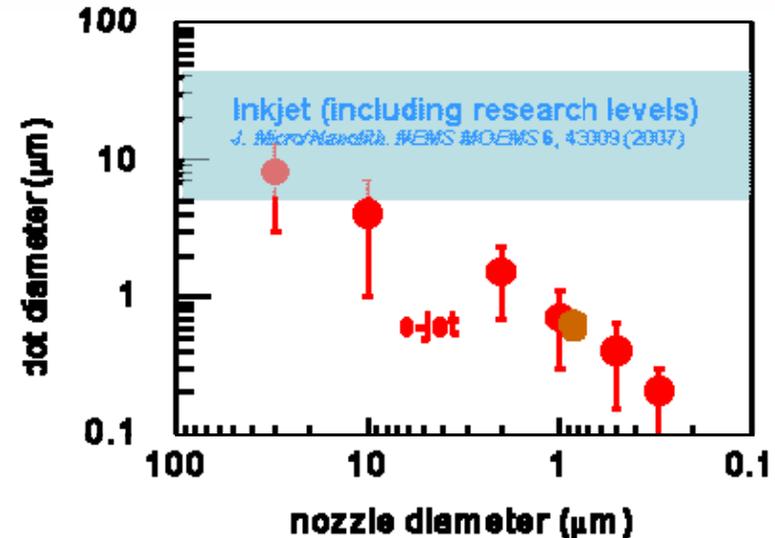
**DNA:** ss-DNA (42-mer) labeled with FL dye (Alexa 546) in 50 mM NaCl / 25 mM potassium phosphate buffer

FL microscope  $\lambda$ :  $560 \pm 40$  nm



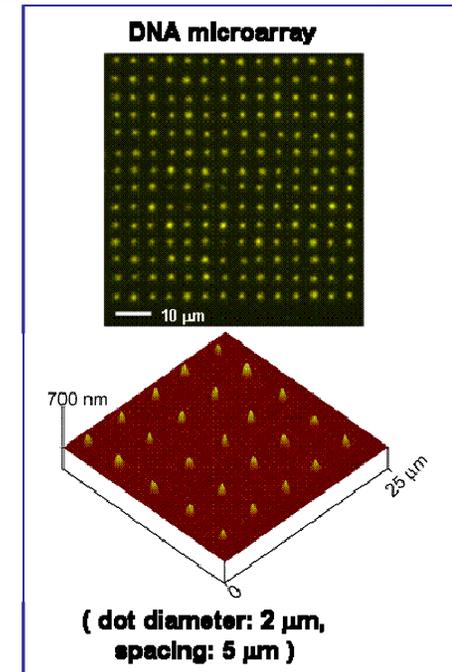
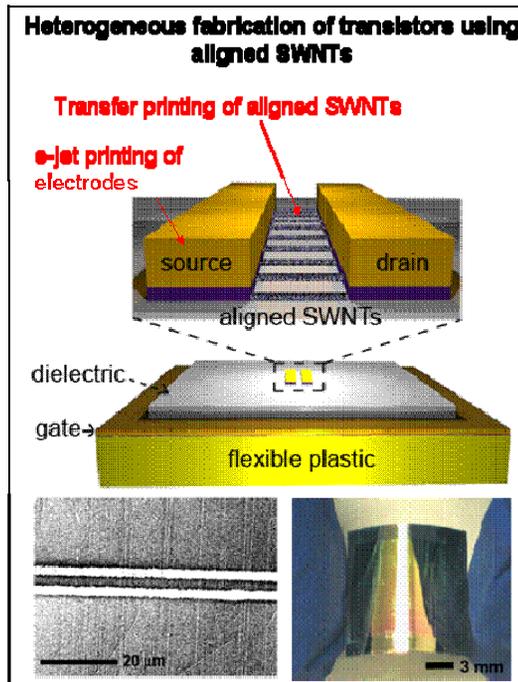
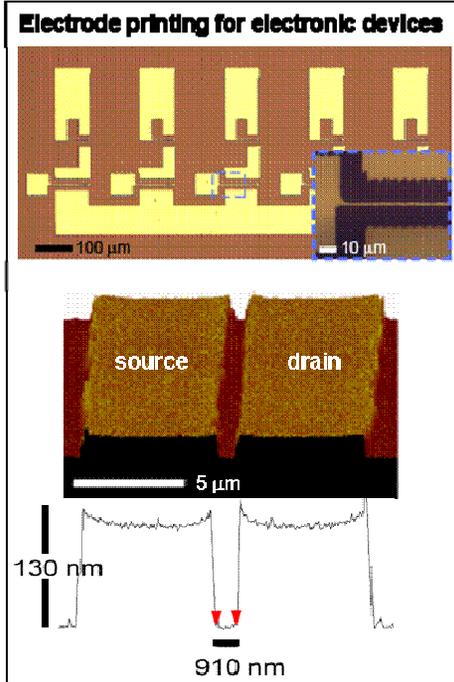
diameter: 1 ~ 2  $\mu$ m using 2  $\mu$ m-ID nozzles

J. -U. Park *et al*, *Nano Lett*, 8, 4210 (2008)

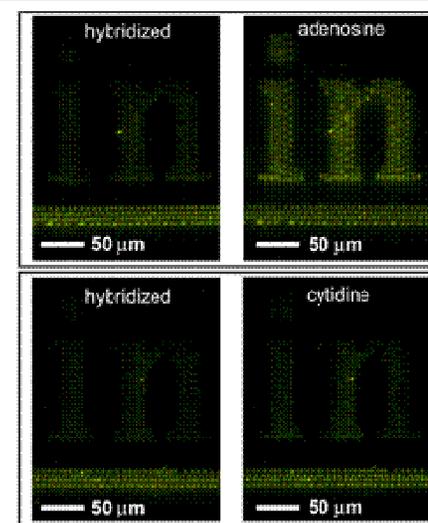
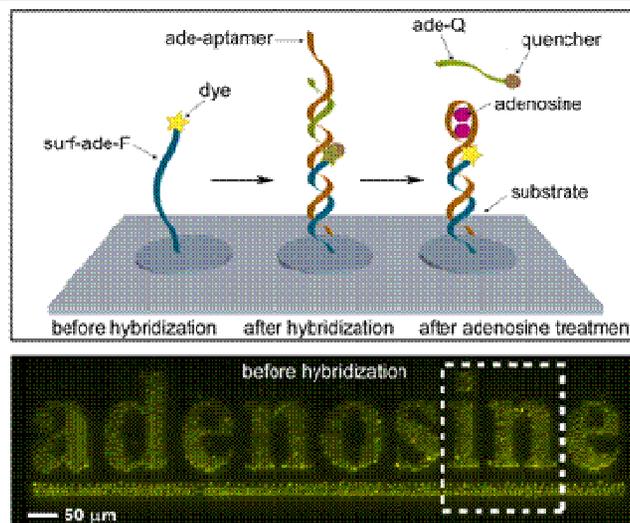




# E-jet Applications



## adenosine sensor



J. -U. Park *et al*, *Nano Lett*, 8, 4210 (2008)

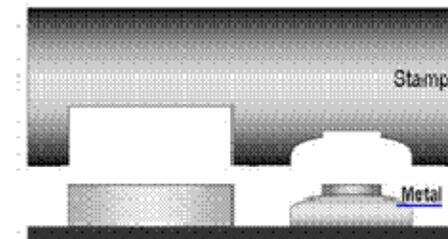
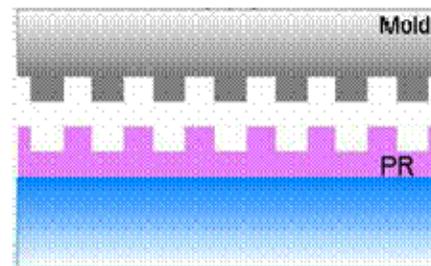
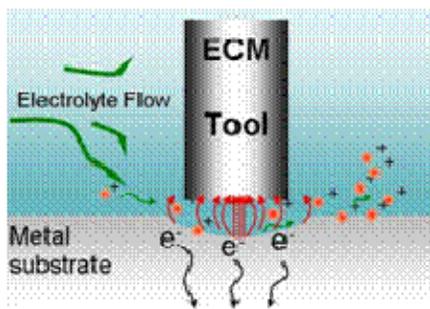
J.-U. Park *et al.*, *Nature Mater.*, 6, 782 (2007)



# Fabricating Metallic Nanostructures



Techniques	Rate	Resolution	Limitations
Damascene		~ 100 nm	<ul style="list-style-type: none"><li>• Resolution</li><li>• Multiple, complex steps</li></ul>
Micro-EDM	~ 3 $\mu\text{m/s}$	> 1 $\mu\text{m}$	<ul style="list-style-type: none"><li>• Resolution</li><li>• Tool wear</li><li>• Substrate heating</li></ul>
Electrochem. $\mu$ -machining	< 1 nm/s	> 1 $\mu\text{m}$	<ul style="list-style-type: none"><li>• Chemical contamination</li><li>• Pattern transfer fidelity</li><li>• Integration with electronic manufacturing processes</li></ul>
Nanoimprint Lithography		< 100 nm	<ul style="list-style-type: none"><li>• Polymeric material only</li><li>• Subsequent processes required</li><li>• PR fracture and de-bonding</li><li>• Residual PR</li></ul>

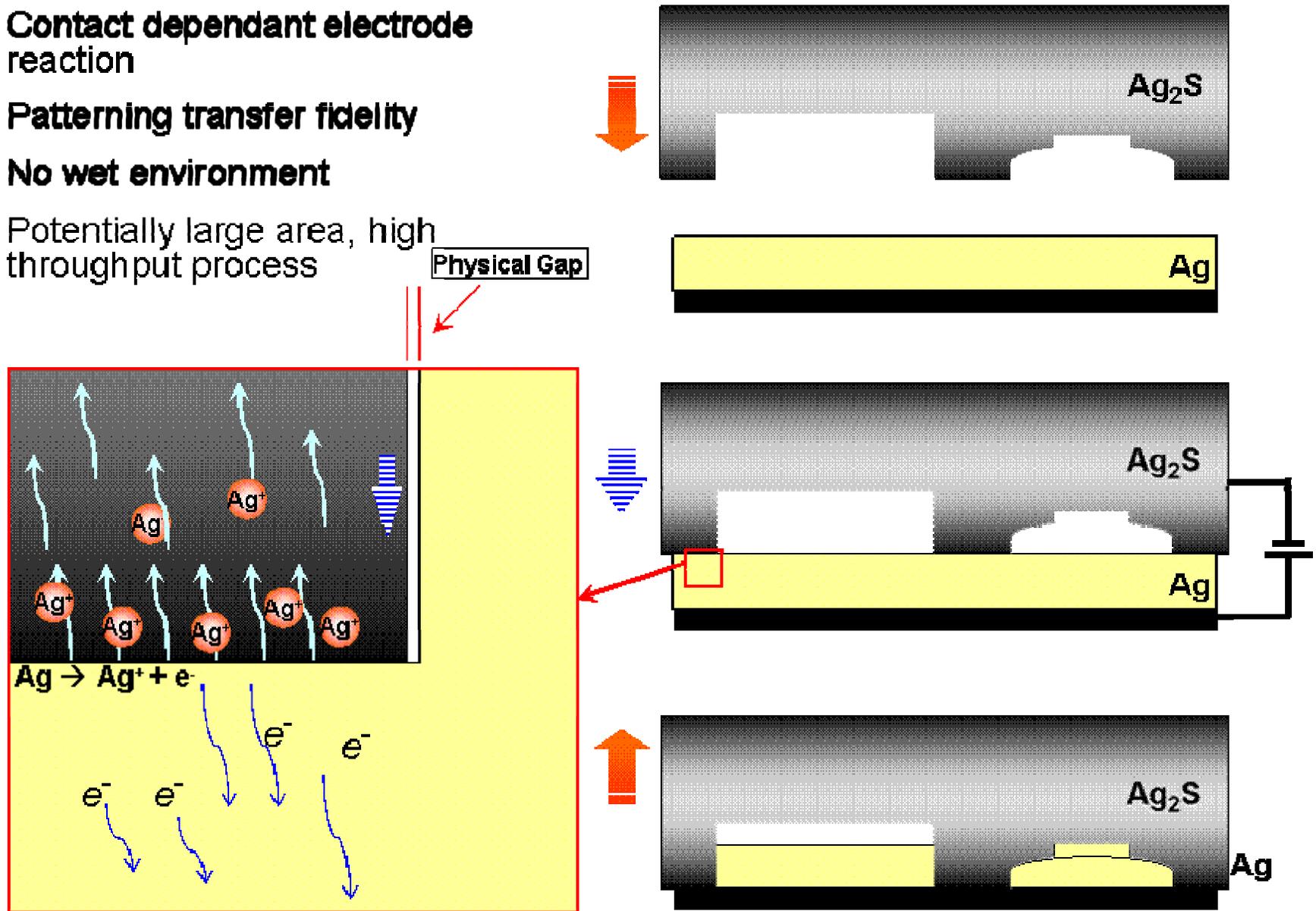




# Solid State Superionic Stamping(S4)

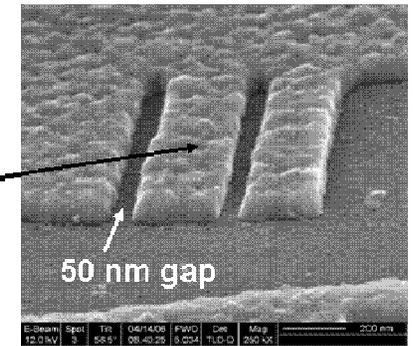
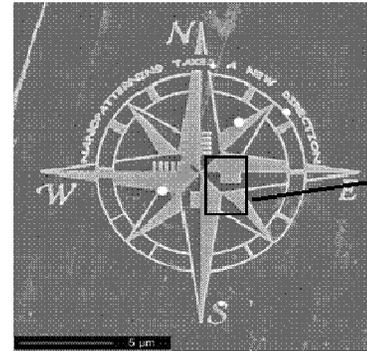
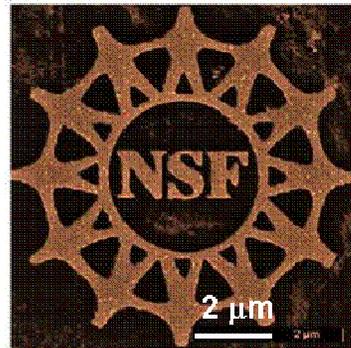
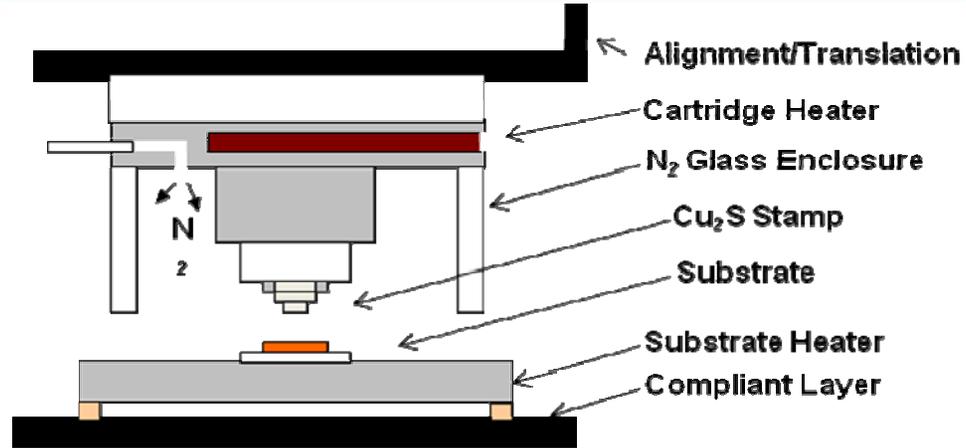
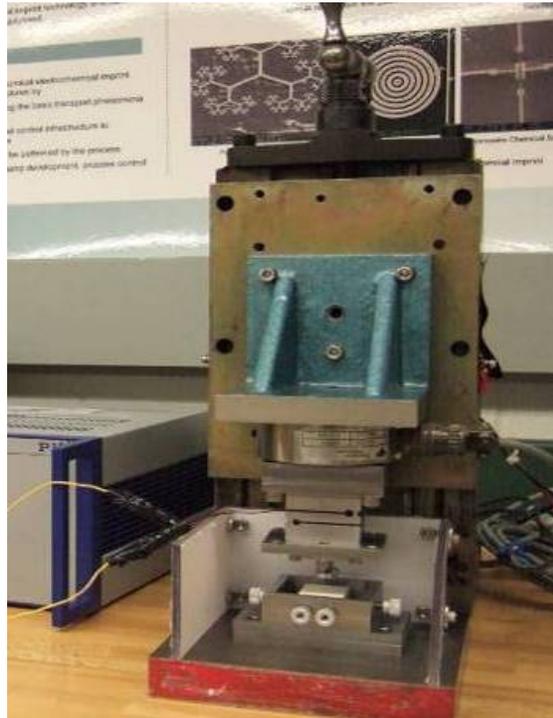


- **Contact dependant electrode reaction**
- **Patterning transfer fidelity**
- **No wet environment**
- Potentially large area, high throughput process

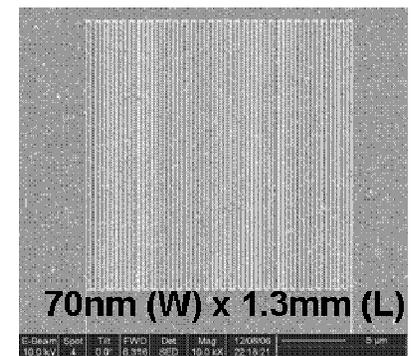
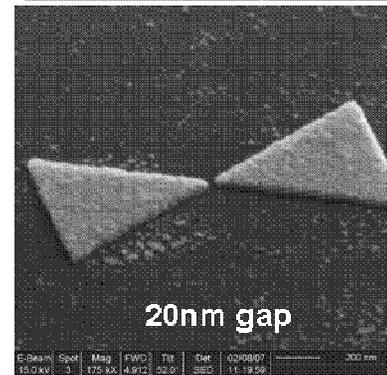
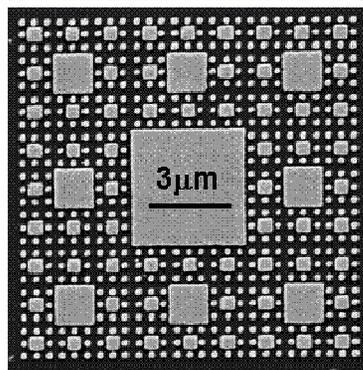




# S4 Tools & Nanopatterns



Simple stamping tools yield sub-50 nm resolutions

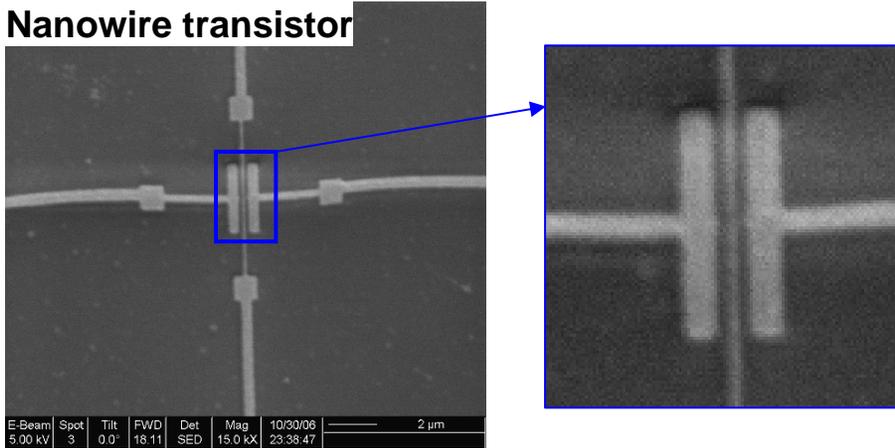




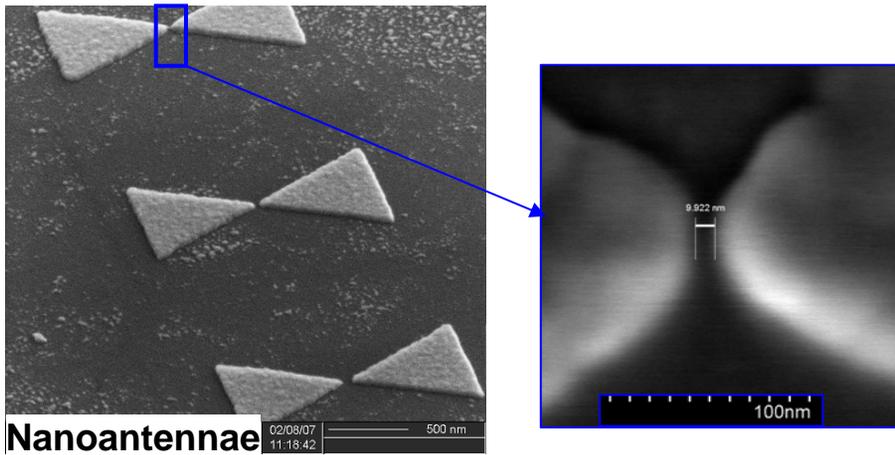
# S4 Rate, Resolution & Repeatability



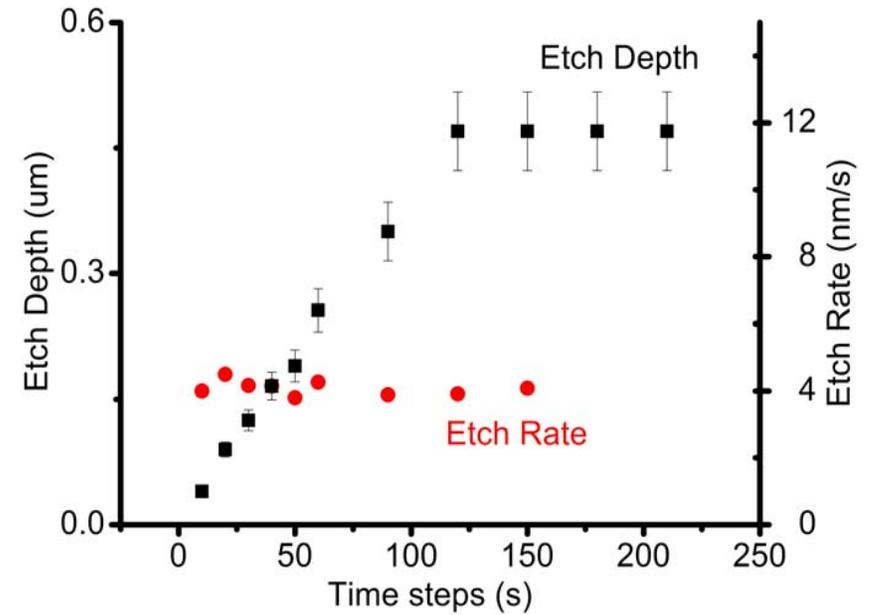
Nanowire transistor



50nm line width achieved with FIB patterning of stamps



~10nm gap bowtie antenna achieved with embossing

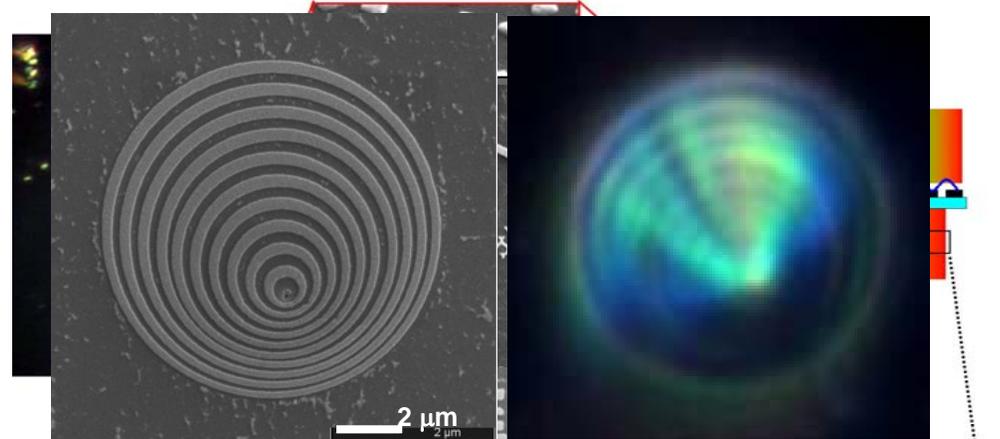




# S4 Applications



- Sensing Substrates
  - Plasmonic (LSPR) Sensors
  - Surface Enhanced Raman Spectroscopy (SERS) substrates
- Interdigitated Electrodes
  - Resistive Sensors
  - Capacitive Sensors
- Nano-Wire Sensors
- Chem-FETS
- Material Tagging & Bar-coding
- Communications
- Photonics



**Gradient index plasmonic lens for photon routing**



**Programmable plasmonic resonance tags at optical wavelength**



# Tooling for NanoManufacturing



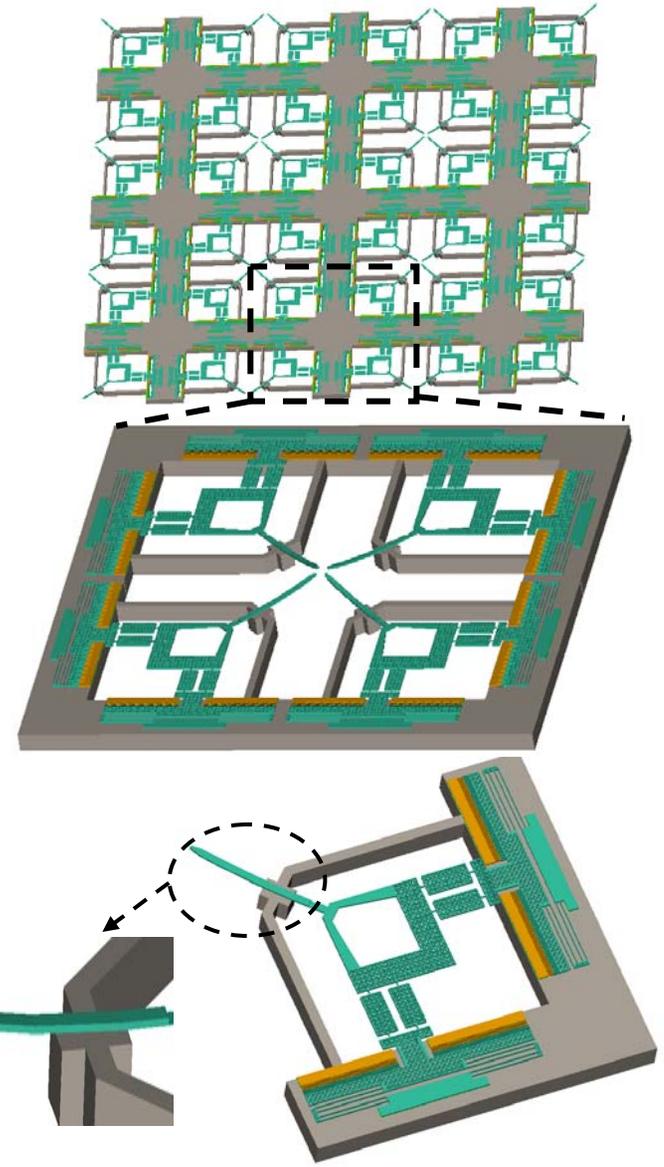
- **Context:** Manipulation, Patterning and Process tools are built at the conventional scale. Bridging several length scales give rise to
  - Uncertainty
  - Susceptibility to environmental noise
  - Lower performance (speeds, for example)
  - Accessibility problems (multiple end-effectors for parallel operations)
- **Needs:** Tooling technology at intermediate scales. For example, MEMS scale tooling that can serve as the scaffolding to get from the conventional scale to the nanoscale



# Micro Scale PKM XYZ Stages

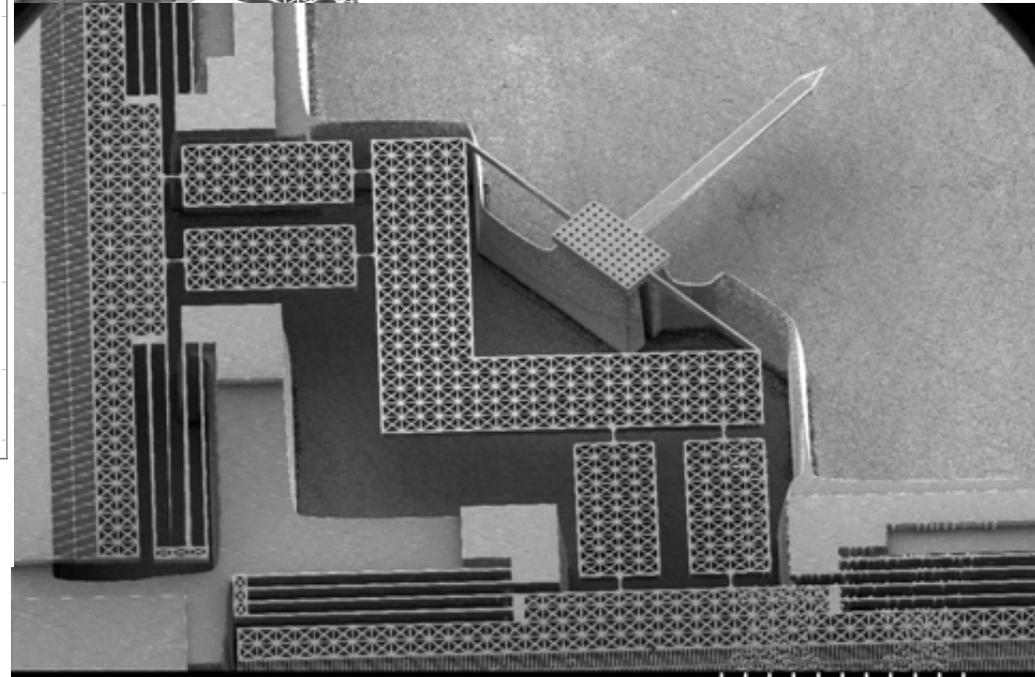
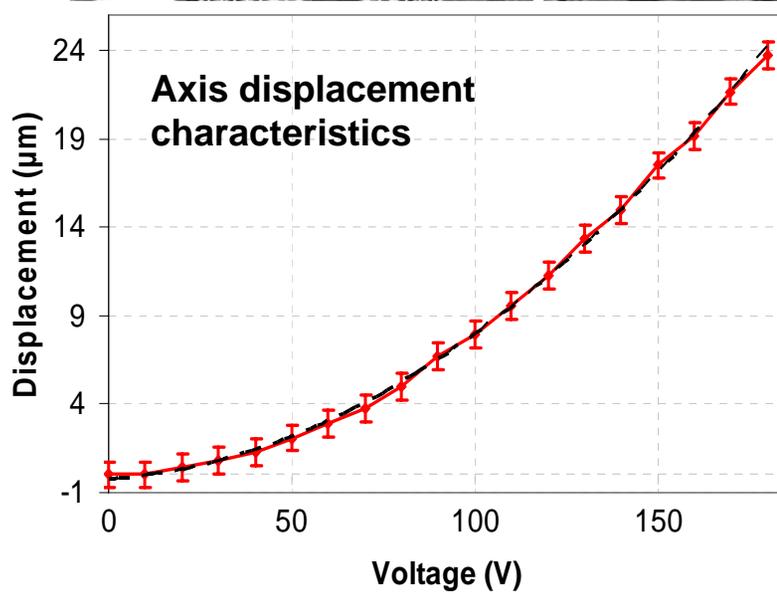
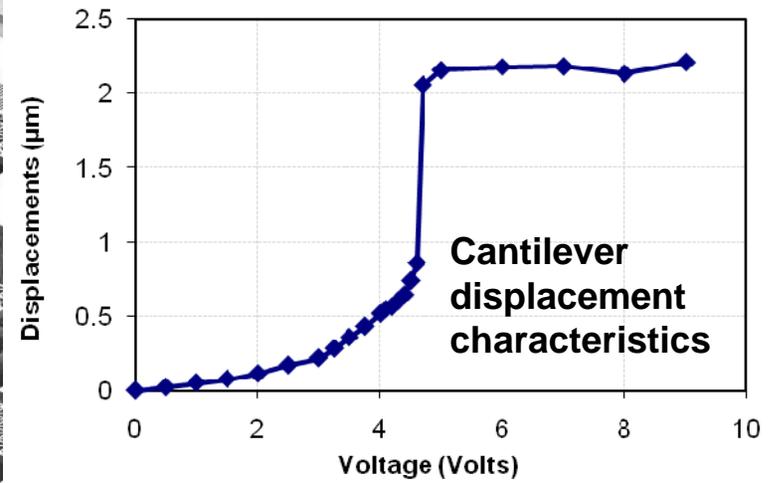
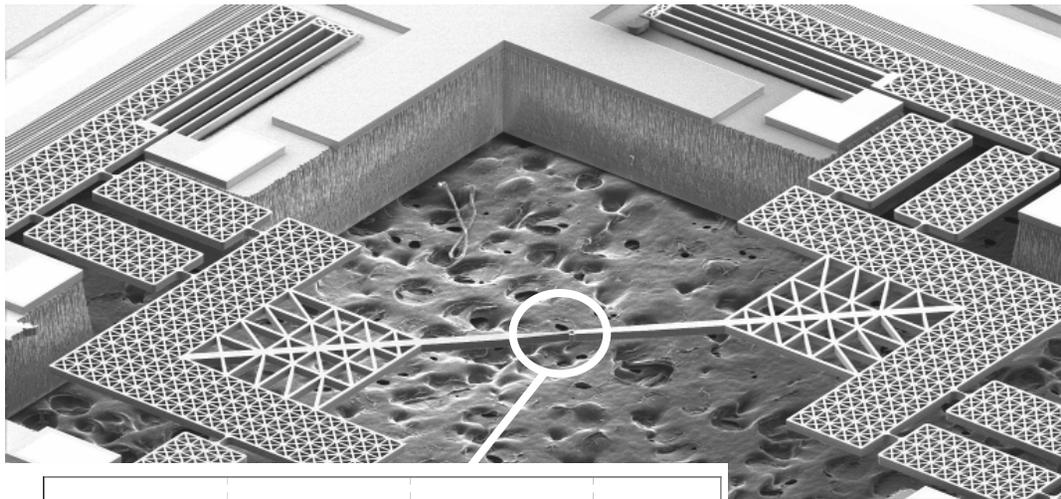


- Why MEMS stages?
  - Seamless integration with other micro/nano manipulators
  - Data storage, micro optical lens scanners, fiber optical switches and aligners,  $\mu$ -force sensor, metrology, in-situ testing, etc.
- Why parallel kinematic designs?
  - Monolithic PKM design works perfectly with MEMS surface micromachining
  - Routing of power to actuators
- Challenges
  - Design
  - Fabrication
  - Sensing & Control





# Towards MEM-Scale Arrays



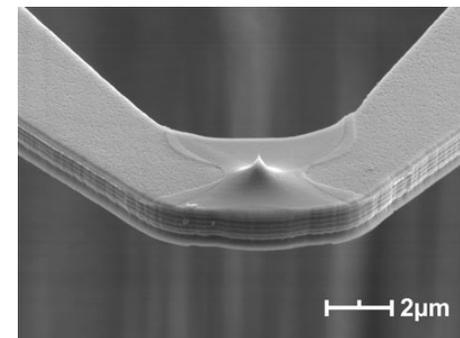
With J. Dong and S. Salapaka



# Sensing for NanoManufacturing



- **Context:** Sensing during nanomanufacturing is difficult because of
  - Accessibility, costs, calibration
- **Needs:** Novel means of combining actuation and processing with sensing
- **Examples:** In cantilever tip-based nanomanufacturing, the cantilever tip is used for processing and sensing.
  - King, for example has developed cantilever tips that perform patterning and thermal sensing



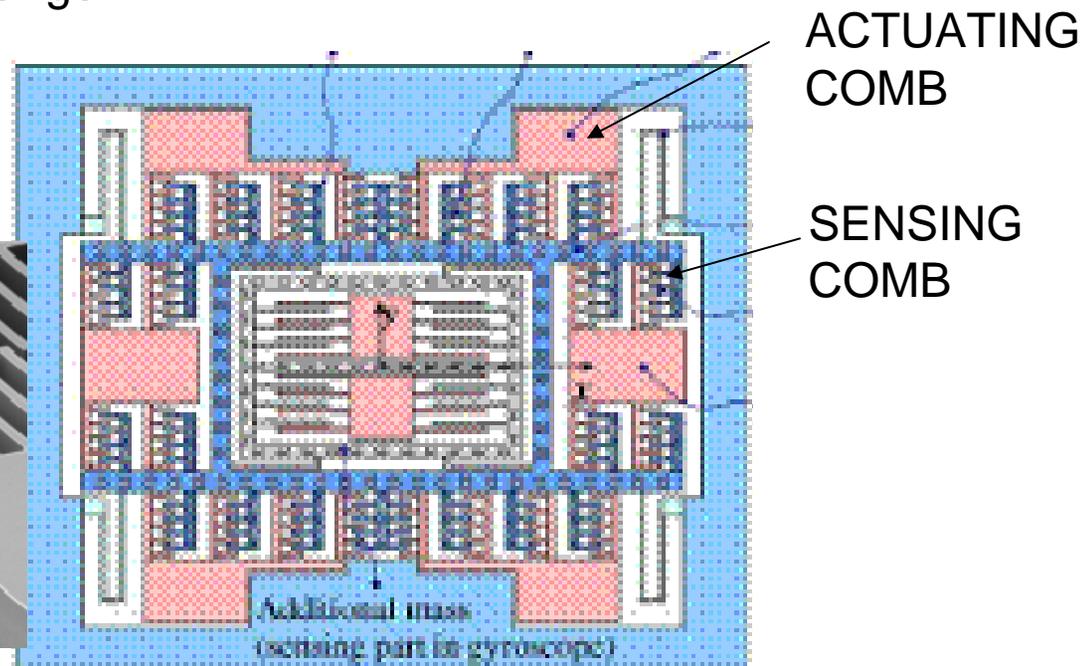
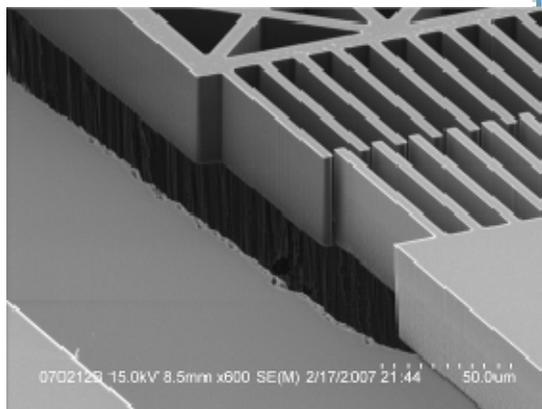
W. King, Nanotechnology, Feb 2009



# Combining Micro- Actuation and Sensing



- Local actuation and sensing at process elements is difficult and expensive.
  - Common approach involves a separate structure for sensing and actuation.
    - Uses precious real estate
    - decrease motion range
    - Decreases yield
    - Increases cost



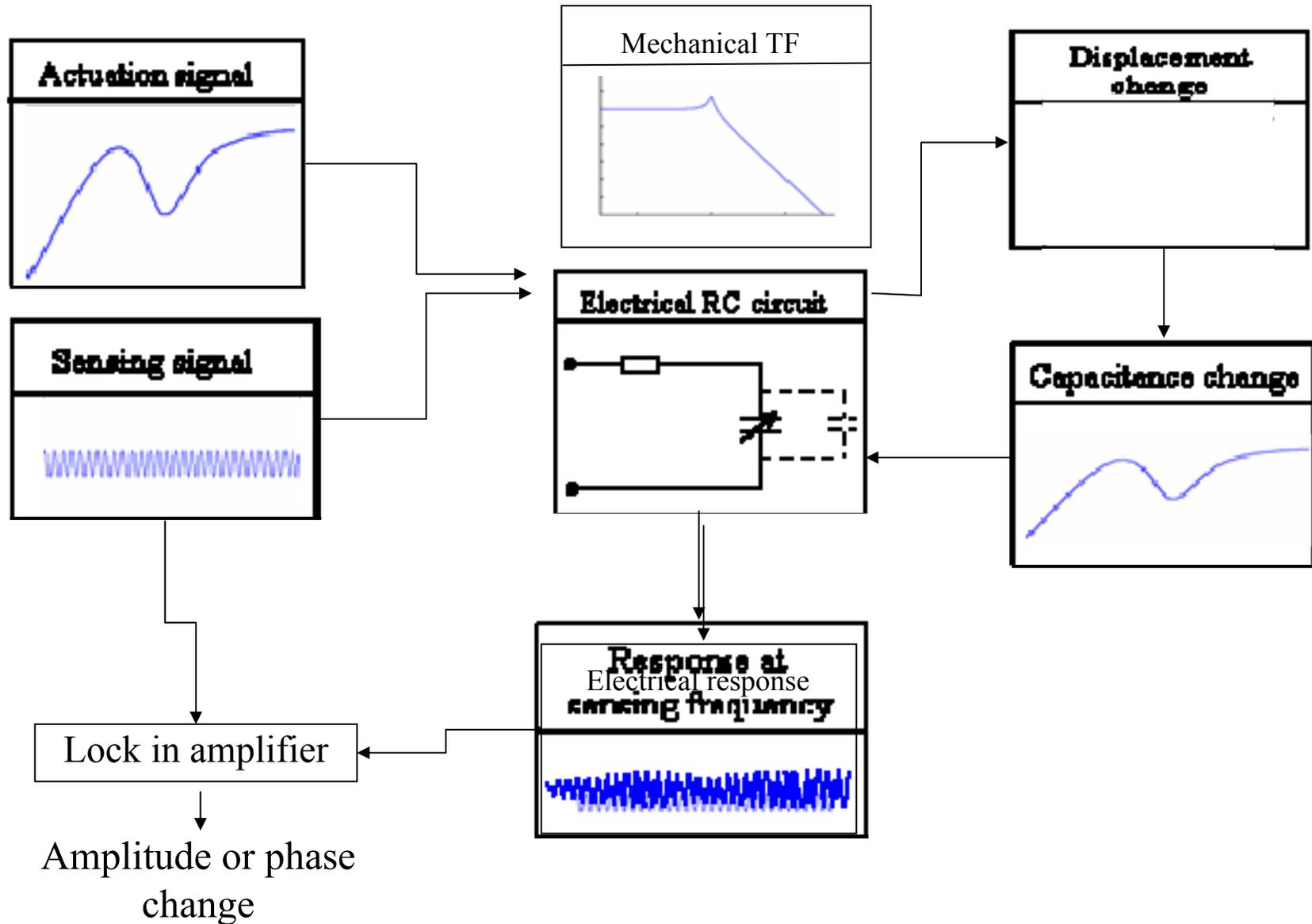
Hee-Moon Jeonga et. al., Sensors and Actuators A: Physical, 2005



- Problem: Crowded Expensive Real Estate
  - Frequency Separation → Low Frequency for mechanical actuation, High for sensing electrical sensing
    - Mechanical transfer function of a electrostatic micro drive is a low pass filter – the drive does not see the high frequency signal.
    - Electrically it is an RC circuit and introduces a phase change to a high frequency signal

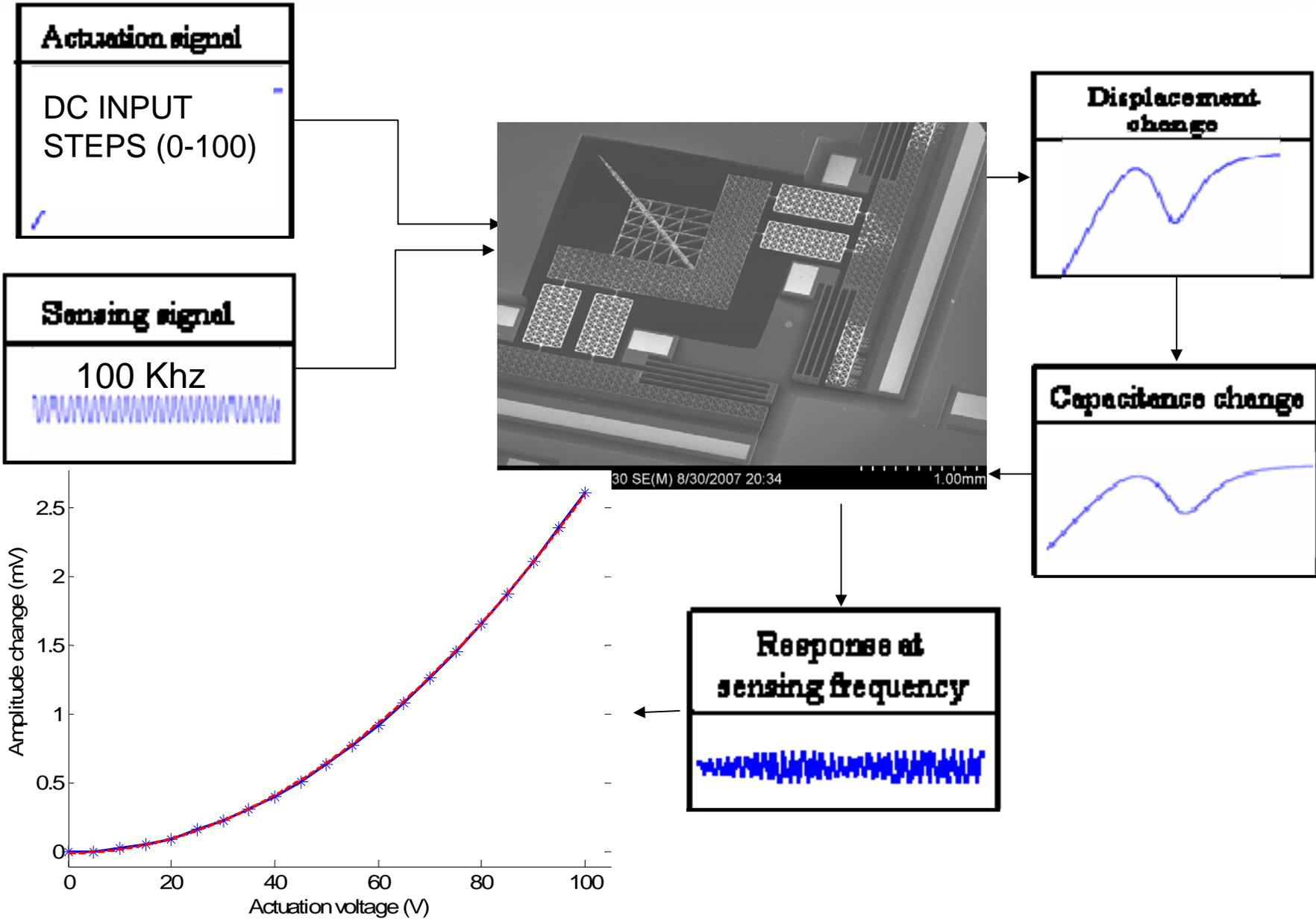


# Sensing & actuating at the micro scale



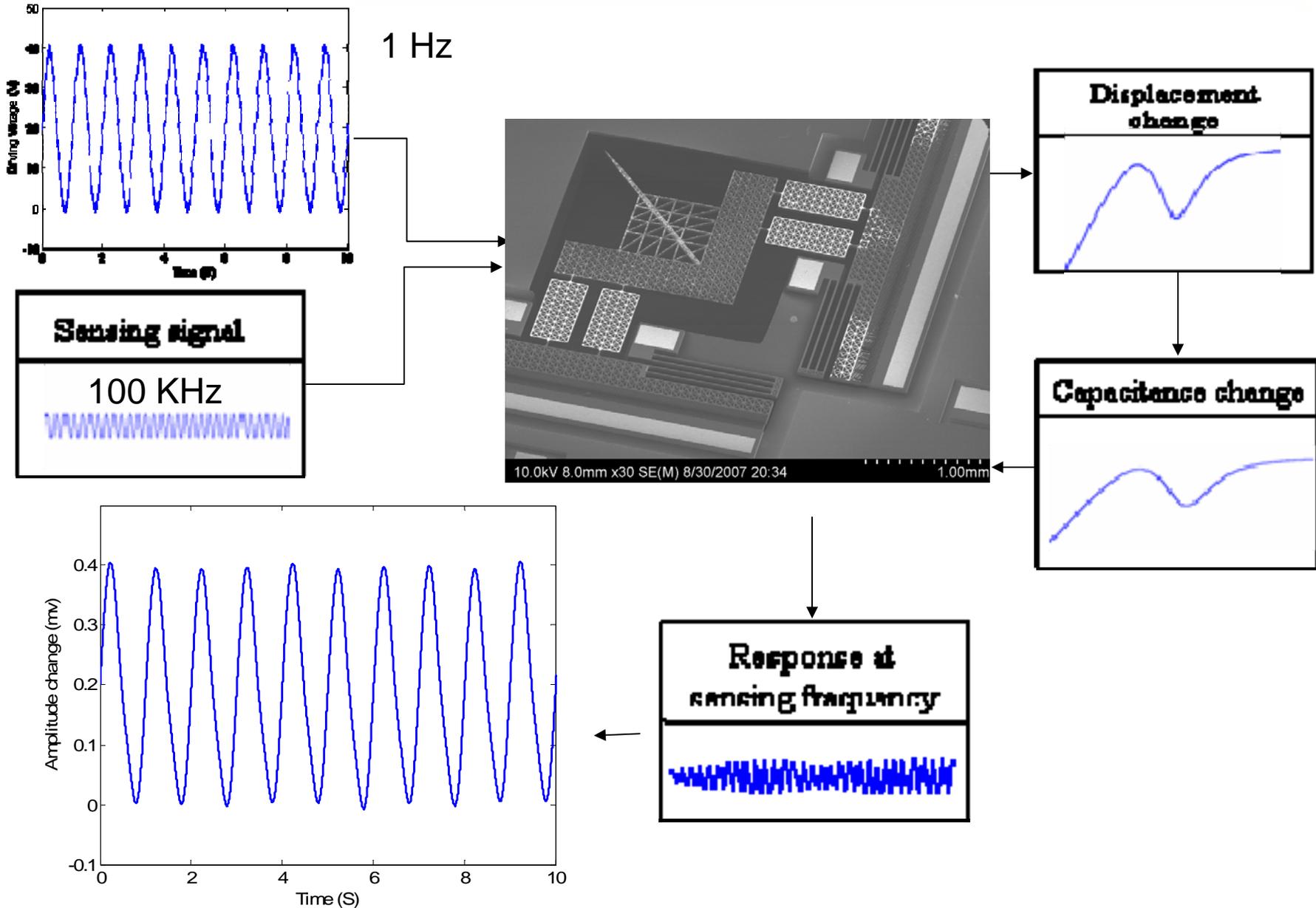


# Sensing & actuating at the Micro scale





# Sensing & actuating at the micro scale

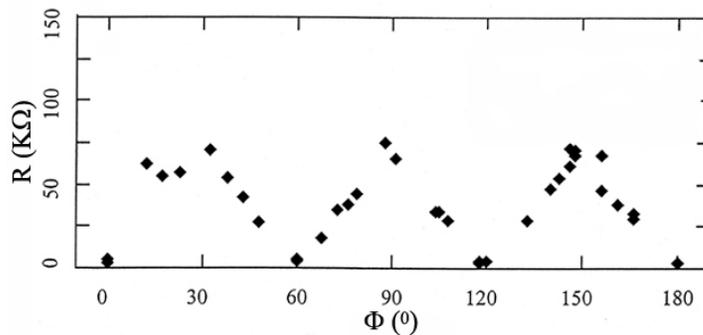
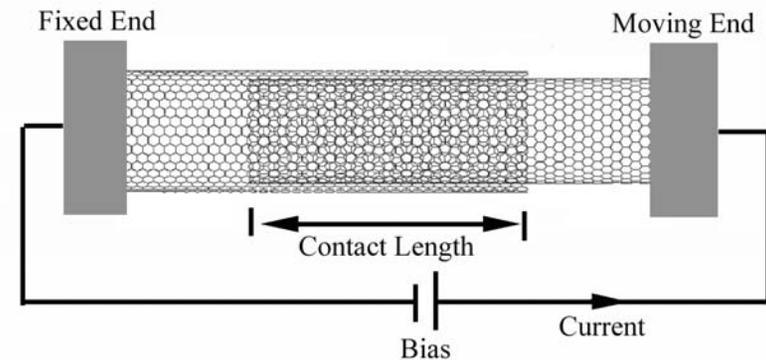
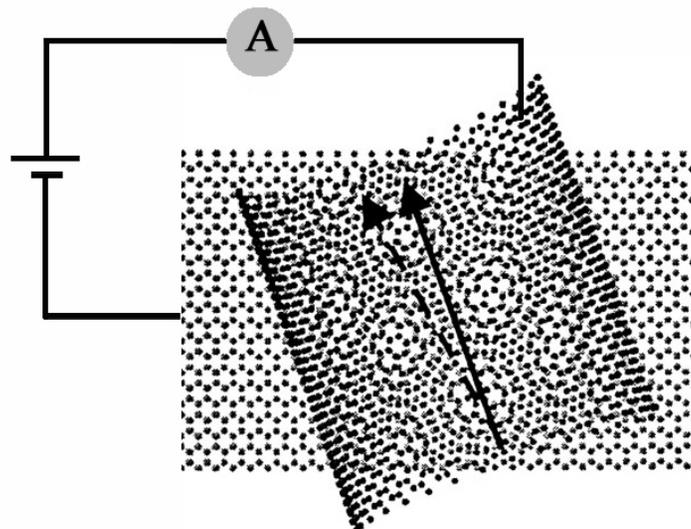




# Size Issue: Nanotube Encoder



Interlayer tunneling conductance in carbon nanotube depends on the interlayer lattice registry



(R. Superfine)

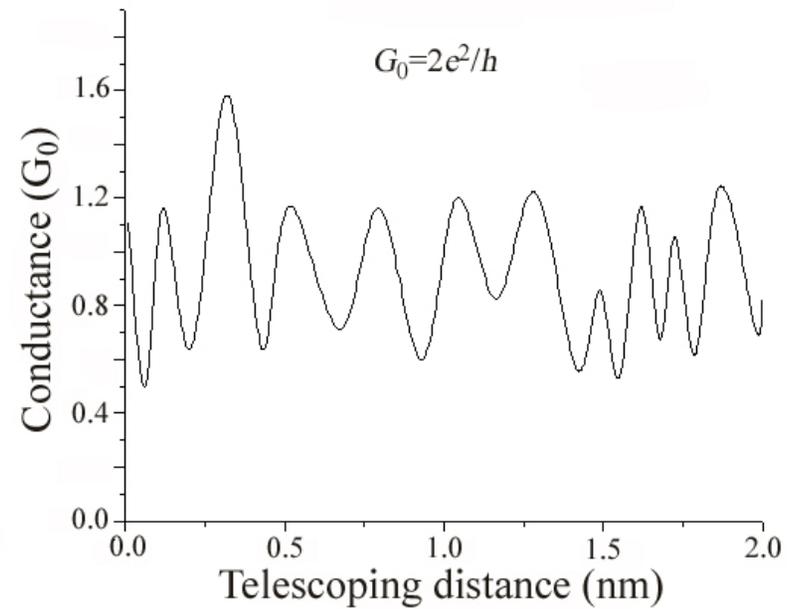
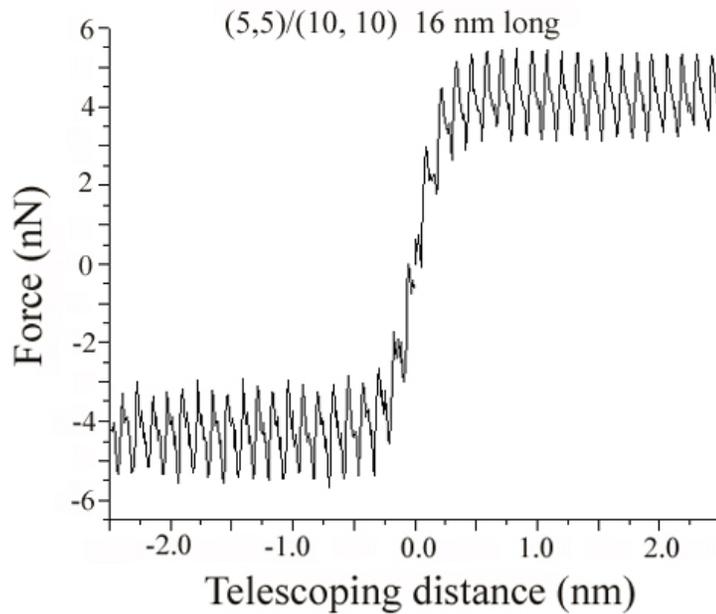
- traceable to a physical constant
- sub-nanometer resolution
- ready-made, friction-free, mechanical guidance system

\* Joint work M-F Yu and Y. Huang

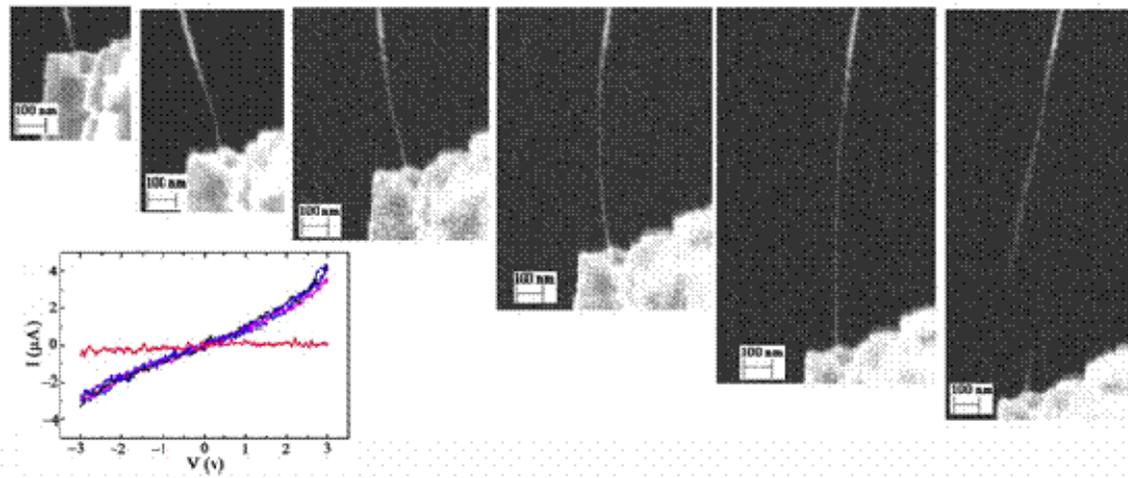




# Nanotube Encoder



(Y. Huang)



(M-F Yu)





# Nanoscale Calibration and Accuracy



- Dimensional calibration at the nanoscale is an increasingly important problem because of difficulties in maintaining traceability because of:
  - Manufacturing, Stability, Registration, and Maintenance Issues
- Multi-step nanofabrication and metrology makes traceability to a common standard an increasingly critical issue



# Calibration Question



- Can self-calibration allow nanoscale dimensional traceability over extended length and time scales ?
  - Accuracy vs. Resolution

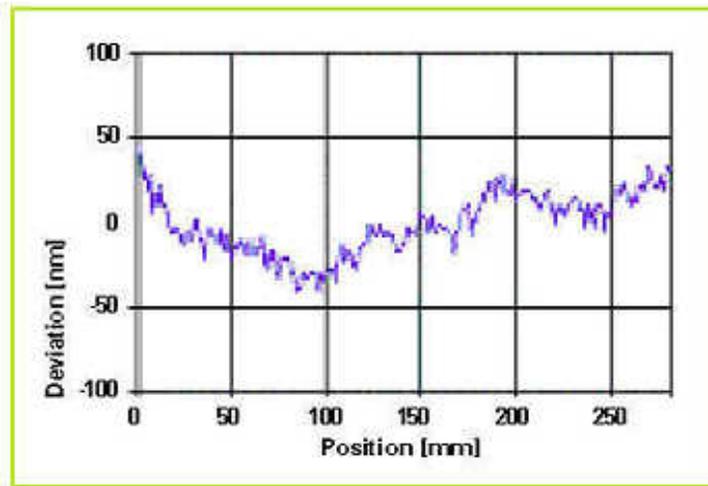
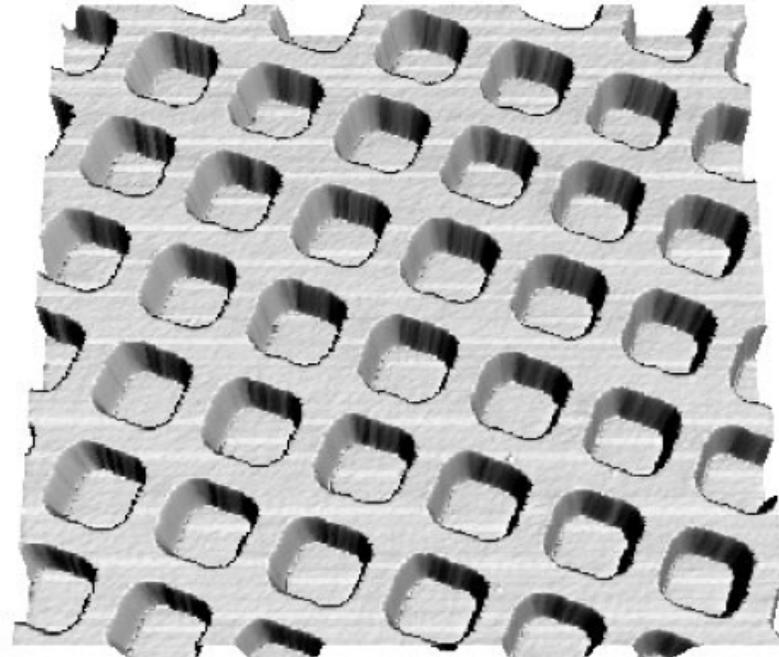


Figure from: Interferential Linear Encoder with 270 mm Measuring Length For Nanometrology by J. Thiel, E. Spanner (<http://www.heidenhain.com/thiel.html>)



**<sup>1</sup>Self-calibration** refers to the use of an imperfectly calibrated measuring instrument and an imperfectly calibrated measurement artifact to improve the calibration of both.

<sup>1</sup> Adapted from: <http://www.interconnect.com/selfcalibration/>

To impart a standard scale, one artifact must include an accurately calibrated measurement.

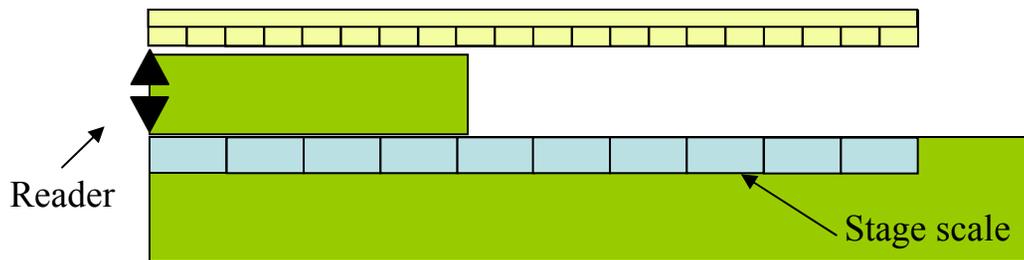


# Self-Calibration, Basic Idea



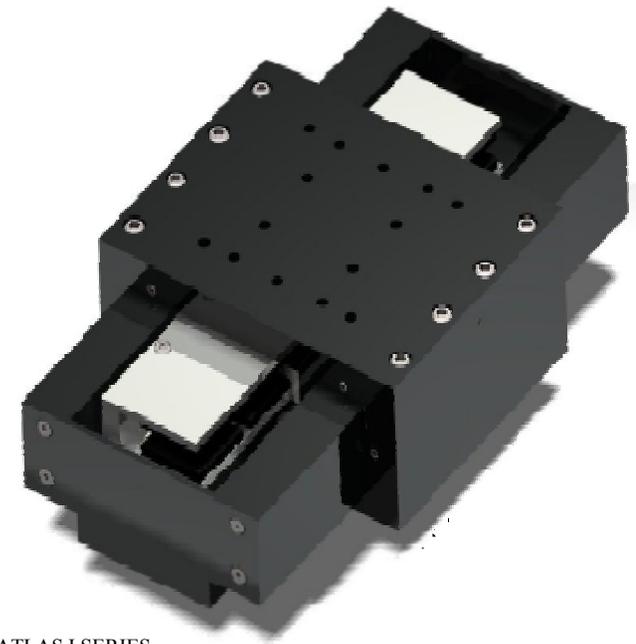
External scale or artifact:

External scale errors :  $s_1, s_2, s_3 \dots s_n$



Stage with an internal scale

Stage errors:  $l_1, l_2, l_3 \dots l_n$



$$o_1 = l_1 - s_1$$

ATLAS I SERIES

Nelson Air ([www.nelsonair.com](http://www.nelsonair.com))

$$o'_{n-1} = l_n - s_{n-1}$$

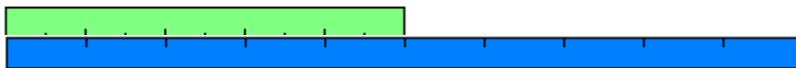
$$\sum s_1 = 0$$



# A self-calibrating stage



Scale Position Relation



$$o_1 = l_1 - s_1$$

$$o'_1 = l_2 - s_1$$

$$o_2 = l_2 - s_2$$

$$o'_2 = l_3 - s_2$$

$$o_3 = l_3 - s_3$$

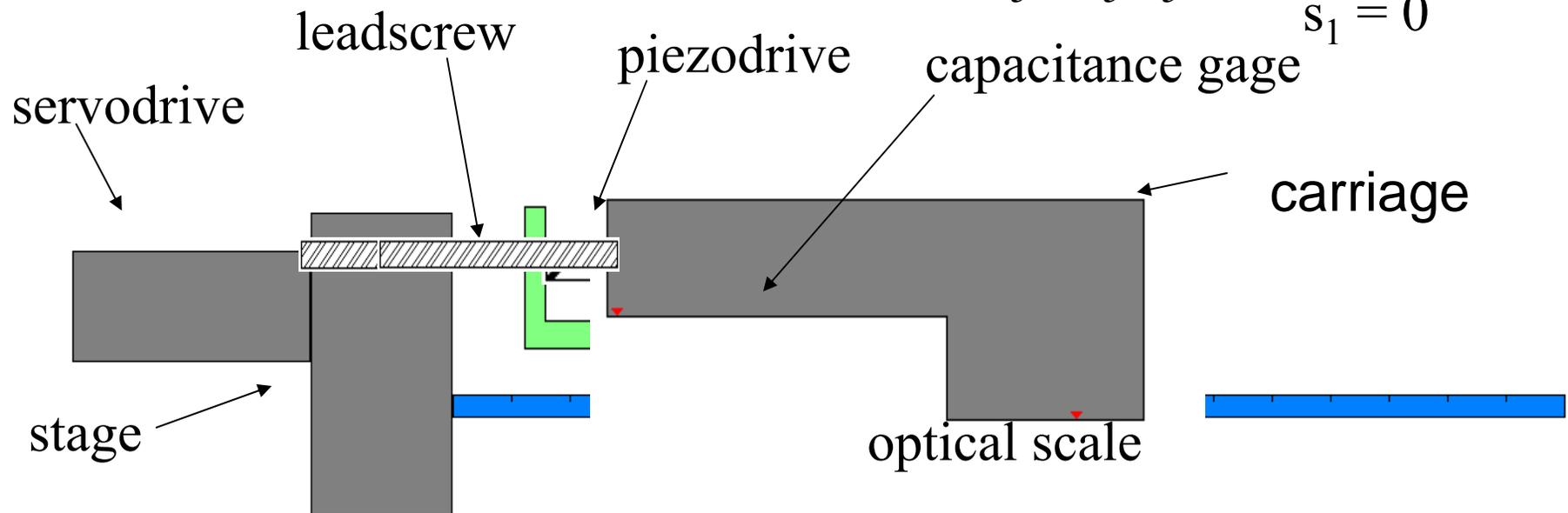
$$o'_3 = l_4 - s_3$$

$$o_4 = l_4 - s_4$$

$$o'_4 = l_5 - s_4$$

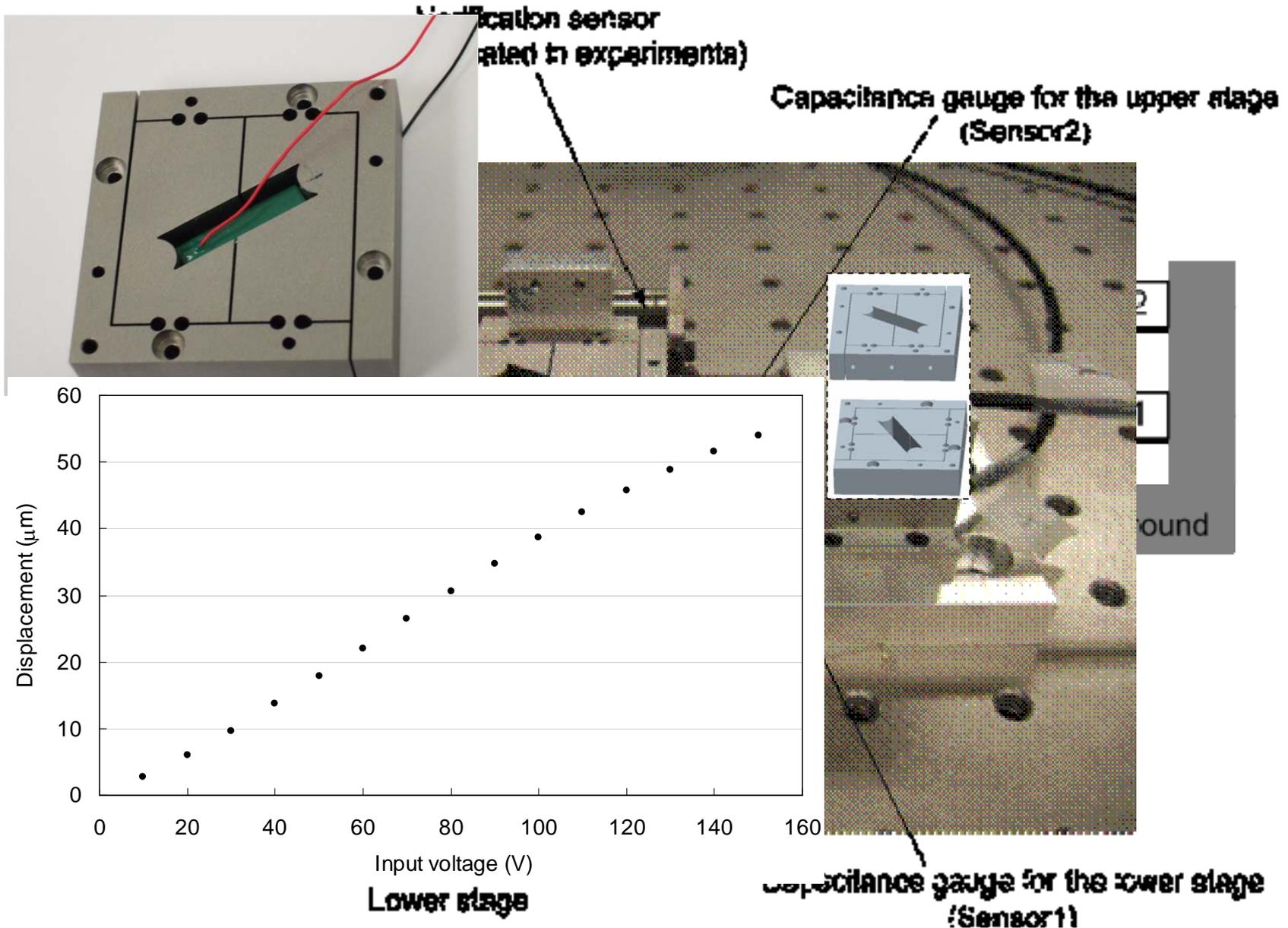
$$o_5 = l_5 - s_5$$

$$s_1 = 0$$



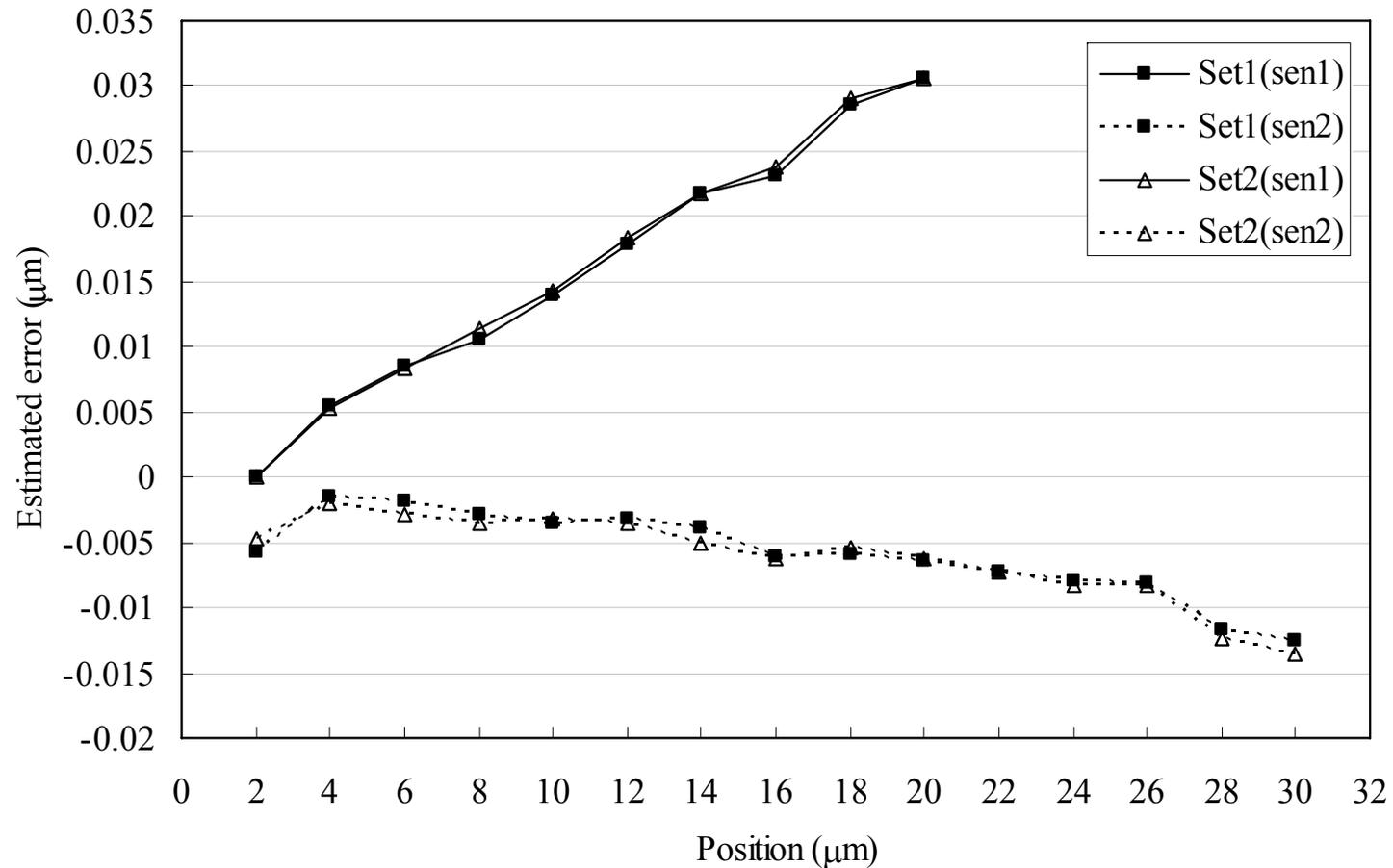


# Self Calibration Experiments





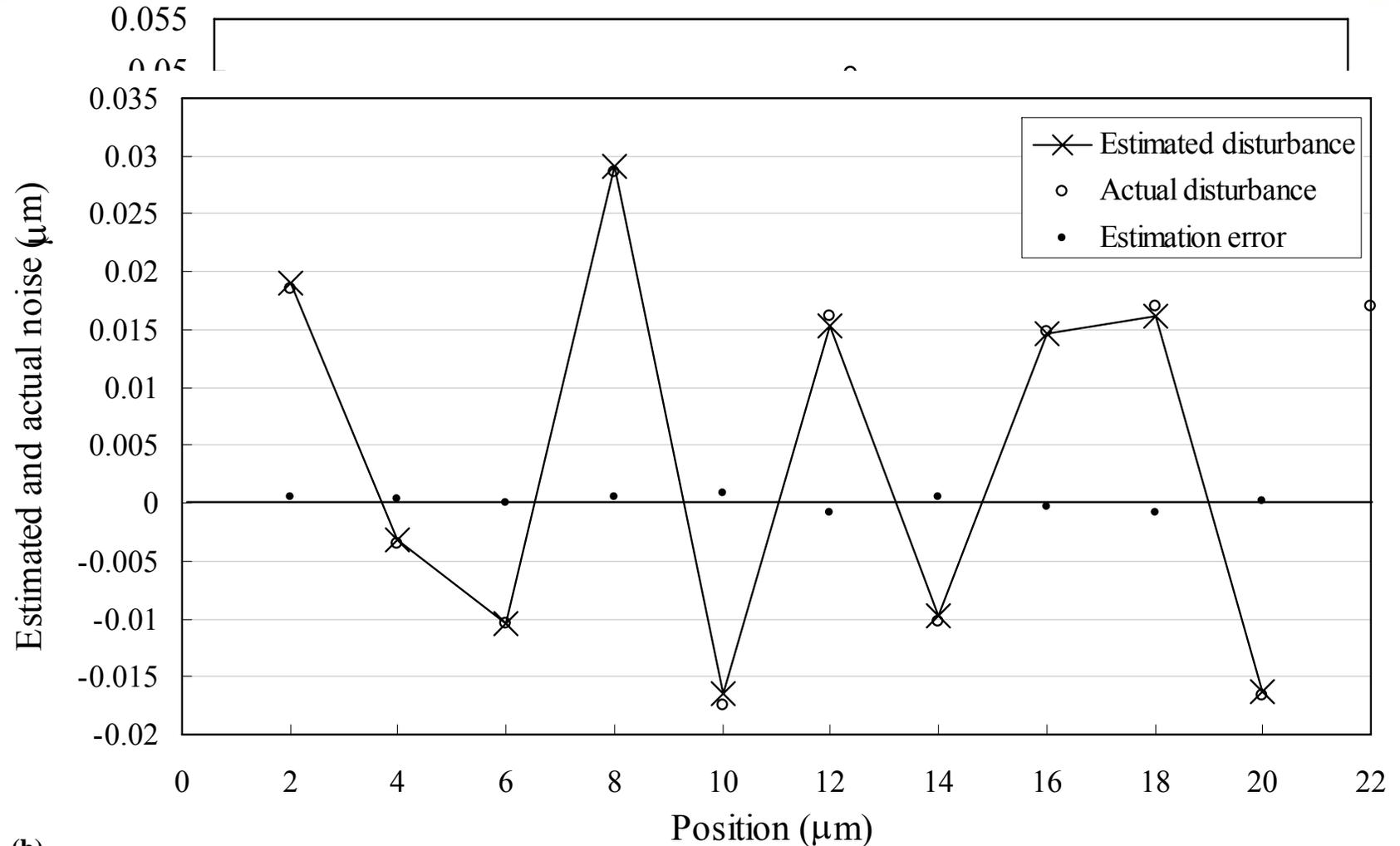
# Self-Calibration Results



Experiments repeated on two different days to verify repeatability of calibration results



# Self-Calibration Result Verification



(b) —x— Estimated Sensor1 error  
- - -x- - - Estimated Sensor2 error

—o— Estimated Sensor1 error with disturbance  
- - -o- - - Estimated Sensor2 error with disturbance



# Integration



- **Context:** Many applications demand that:
  - Nanostructures be assembled over large areas
  - Integrated multiple functions
  - Involve vastly dissimilar materials that may not be processable together
- **Need:** Process technology for the *heterogeneous integration of functional nano- and microstructures*

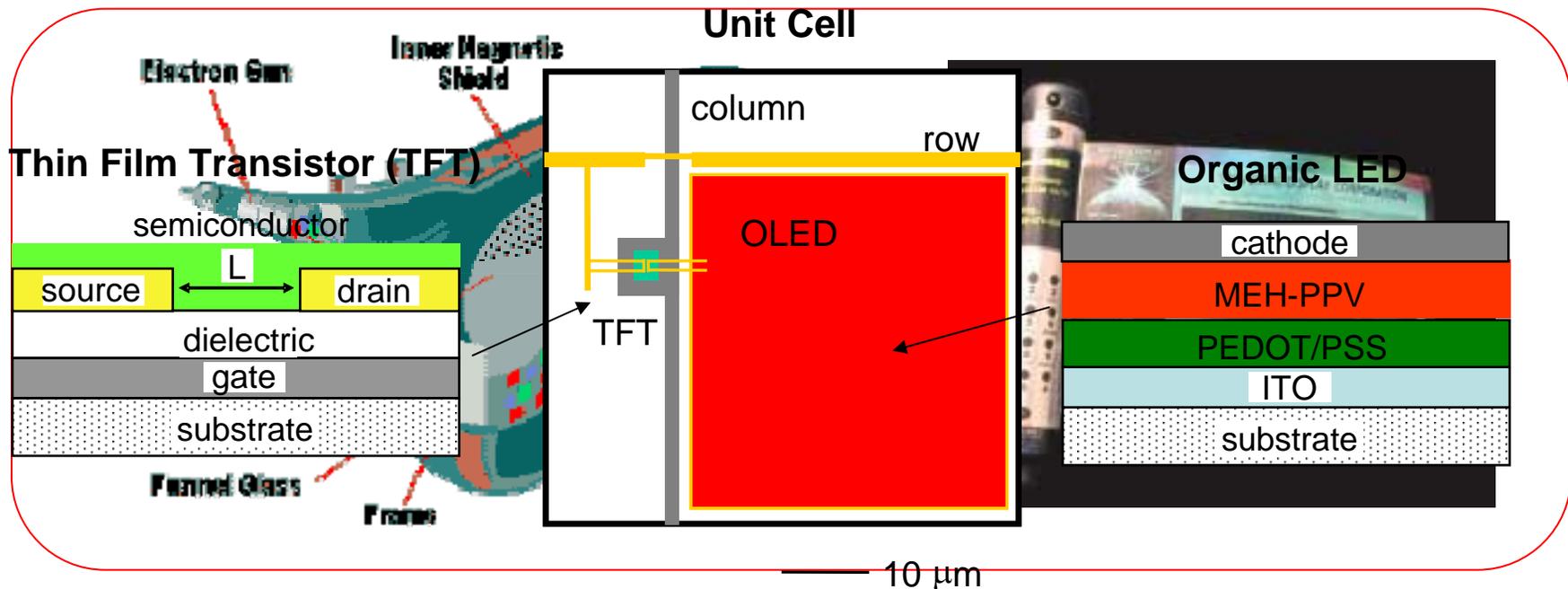


# Heterogeneous Functional Integration



Emerging Paradigm in New Product Development

- Heterogeneous Integration of functions into products rather than 'assembling' them



- Here electronic, mechanical and optical function are integrated into each 10 micron unit cell.



# Heterogeneous Functional Integration



**Logic and Switching: Single Crystal Silicon**

**Vision: InP/SCS**

**Communications: Cu/Fe/Co**

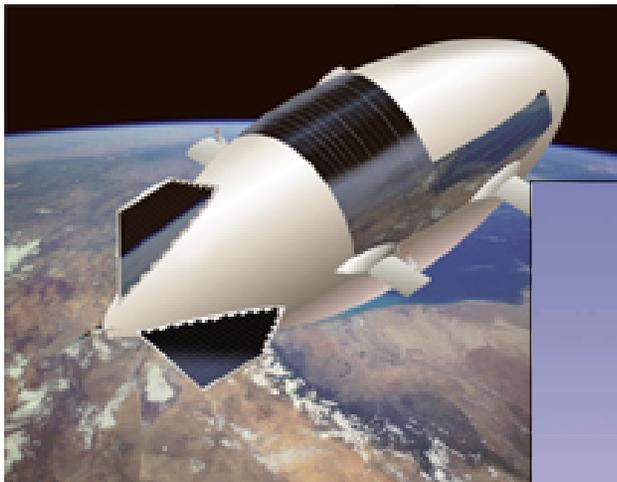
**Energy Collection: SCS/GAs**

**Energy Storage: Lithium Ion Polymers**

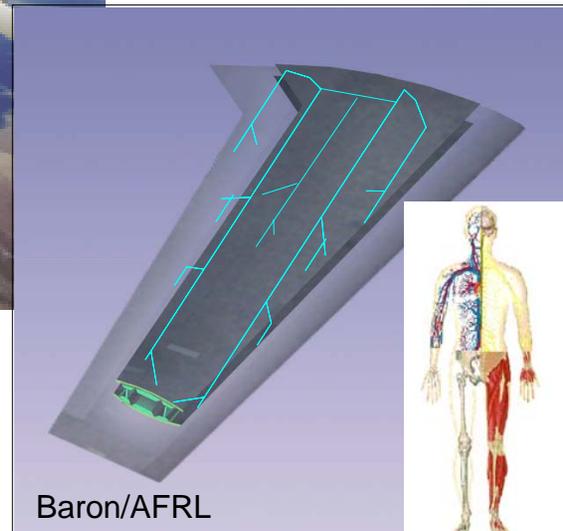
**Actuation: PZT/Ionic Polymer Composites**

**Chemical Sensing: Platinum/Nickel**

**Mechanical: Polymer materials**



**Stretchable Electronics**



**Living Airframe**

**Foldable Communications**



**Folded for transport**

**John Rogers**



# Heterogeneous Functional Integration



- Miniaturization, like in electronics, but with many different materials to address different functions.
- Unusual physical form factors such as large areas, flexible, stretchable, transparent
- Involves multiple scales

Intelligent, Wireless  
Medical Sensors



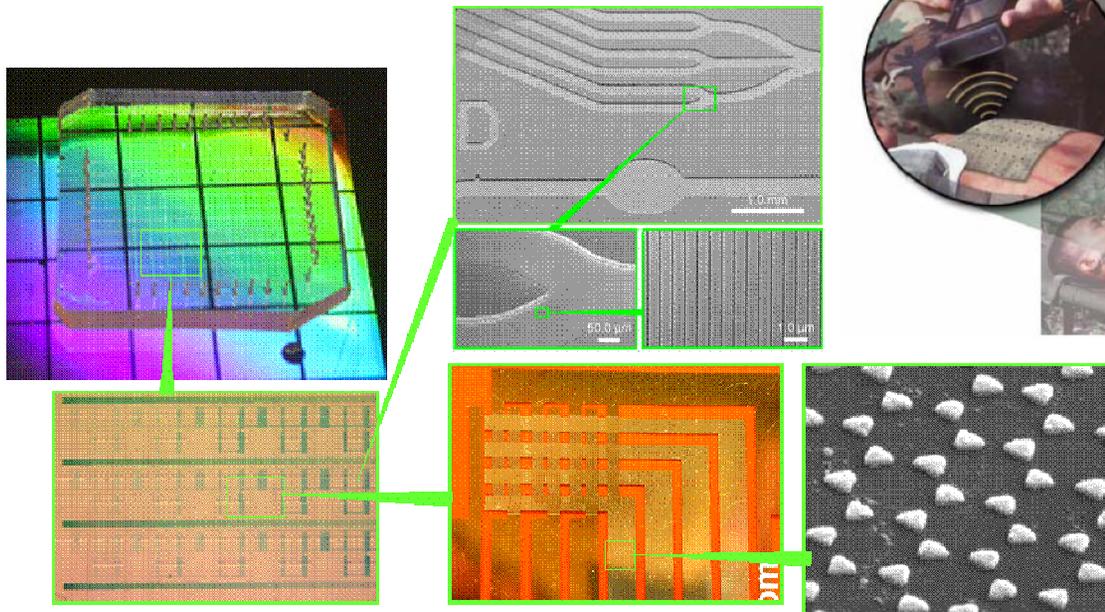
Smart Surgical Glove

$\mu$ sensors:  
chemical,  
optical,  
thermal

$\mu$ fluidic  
channels

embedded  
integrated circuits

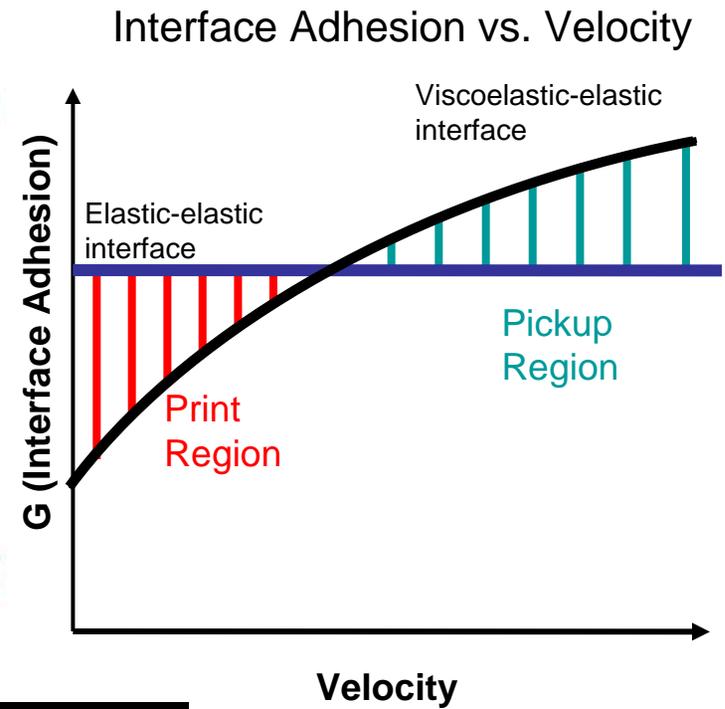
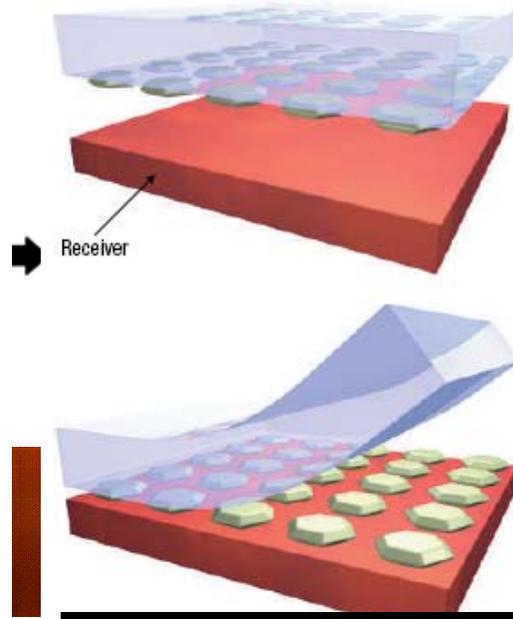
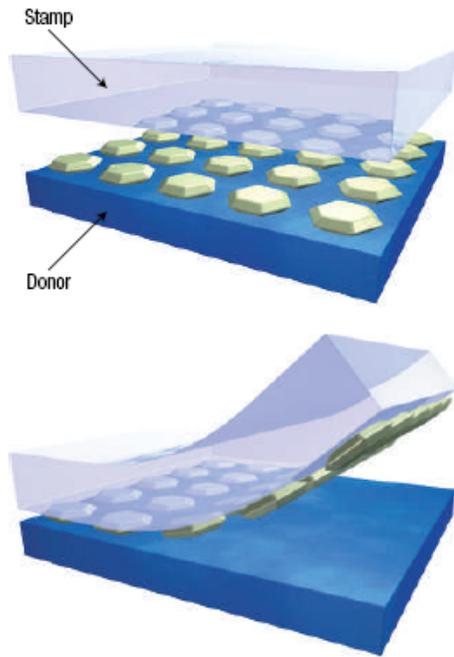
RF transmit/receive



Lab-On-A-Chip



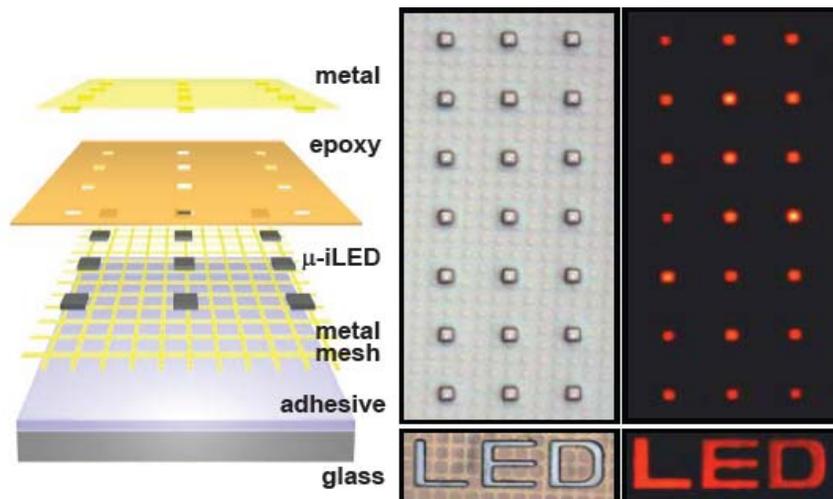
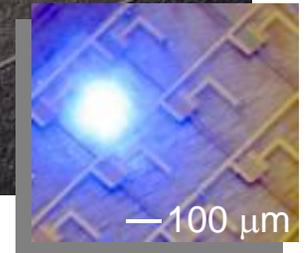
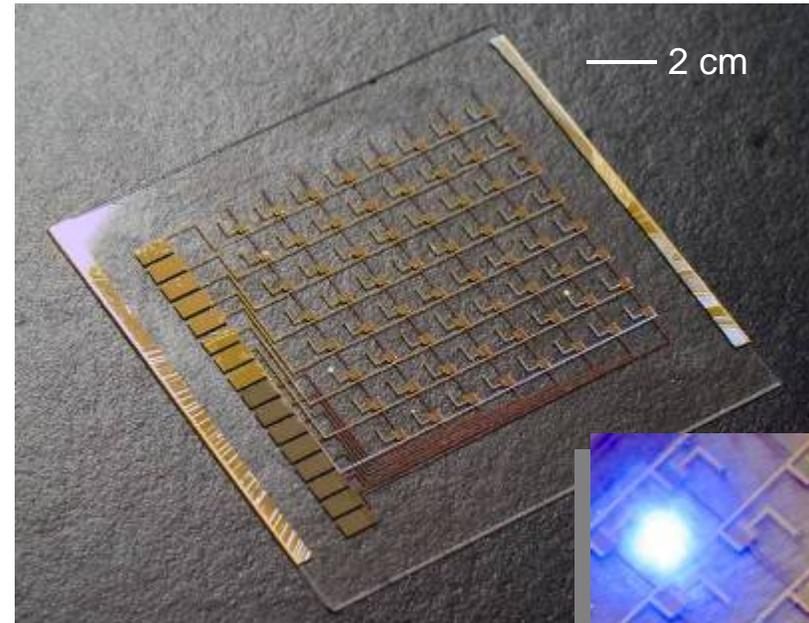
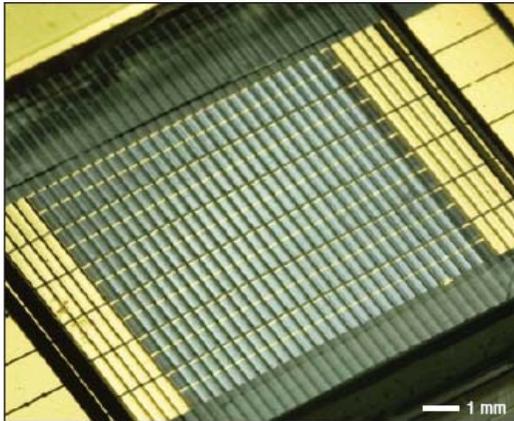
# Transfer Printing



Rogers



# Heterogeneous Integration Examples



J. Rogers

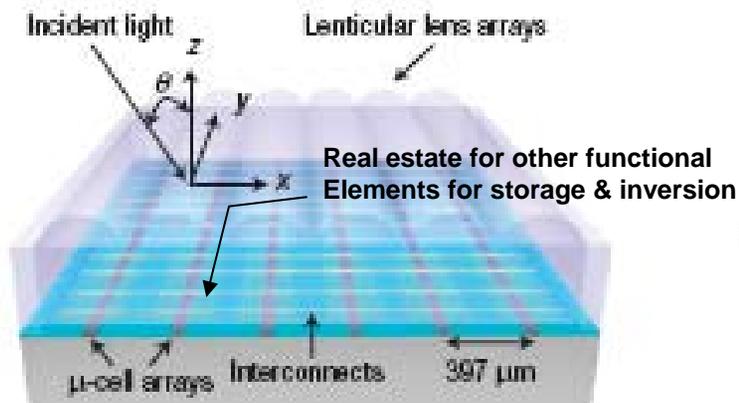


# HI for Energy Applications



- Reduce the c-Si (or other active materials) by 2 or 3 orders of magnitude
- Integrate multiple functions and create scalable manufacturing approach

## CONCEPT

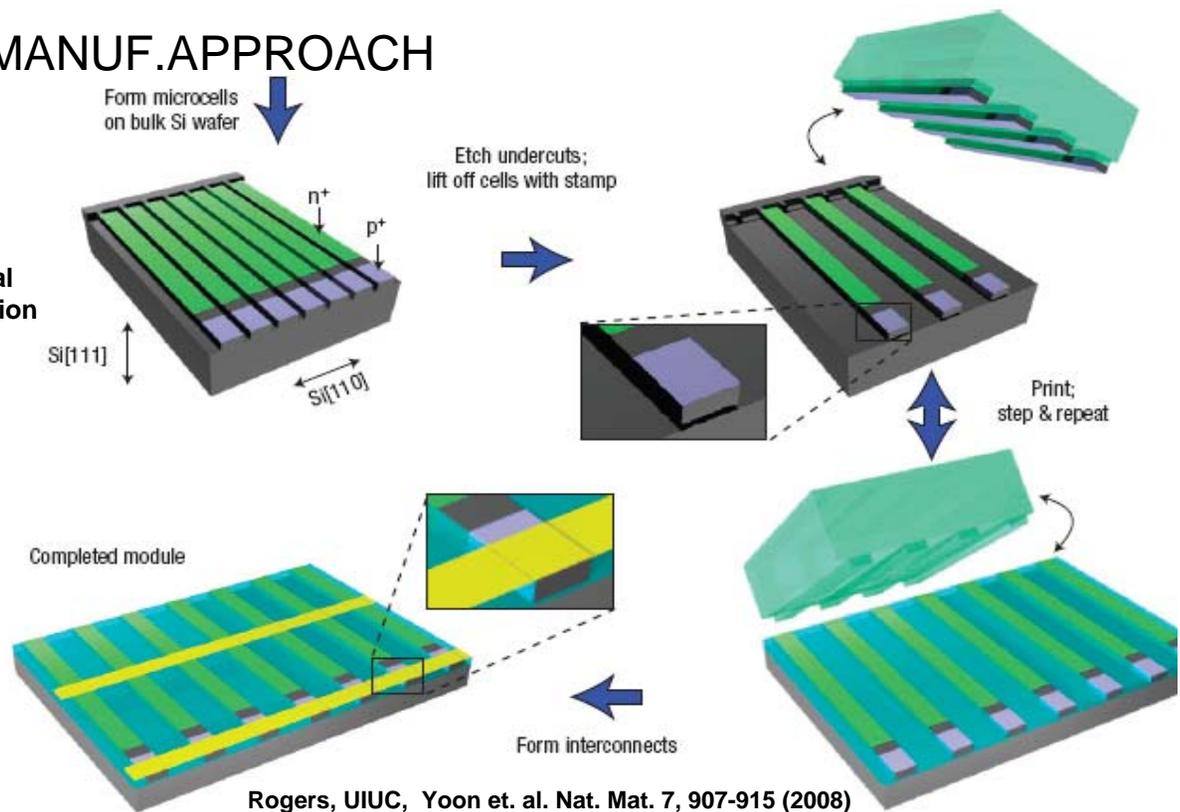


Rogers, UIUC, Yoon et. al. Nat. Mat. 7, 907-915 (2008)

## CHALLENGES

- Scale up of Manufacturing
- Materials Design
- Thermal Management
- Reliability

## MANUF. APPROACH



Rogers, UIUC, Yoon et. al. Nat. Mat. 7, 907-915 (2008)



# Summary



- We have examined some of the issues and challenges in realizing scalable and robust manufacturing at the nanoscale.
- The examples were not meant to suggest that comprehensive solutions are available for these challenges.
- Many other issues, non-technical and technical, such as workforce development, public perception, investment in manufacturing, modeling and simulation, etc. need to be addressed.
- Interesting problems that require classical and non-classical approaches
- Knowing the domain is extremely important
- Systems are still small, but scale-up is imminent and robustness and yield issues will dominate research

# Can Polymer Self-Assembly Transition from Si-Wafer Based Technology to a Reliable, High Volume Roll-Roll Manufacturing Platform for Low Cost Devices?

Jim Watkins

Center for Hierarchical Manufacturing – NSF NSEC  
Polymer Science and Engineering Department  
University of Massachusetts, Amherst

# Today's Discussion

- Highlights from NSF Workshop on Research Challenges for Integrated Systems Nanomanufacturing
- A Snapshot of the Center for Hierarchical Manufacturing
  - including recent advances relevant to today's discussion
- Can Self Assembly be Adapted for Low Cost, High Volume Production of Devices via Roll-to-Roll Processing?

# NSF Workshop on Research Challenges for Integrated Systems Nanomanufacturing

February 10-11, 2008

*Workshop organizing committee:*

Prof. James Watkins, University of Massachusetts Amherst

Prof. Mark Tuominen, University of Massachusetts Amherst

Prof. Mario Roteo, University of Massachusetts Amherst

Prof. Abhi Deshmukh, Texas A&M University

**Goal: To elucidate the key research challenges facing Integrated Systems Nanomanufacturing, thereby providing a roadmap of the near term and long term focus areas that must be addressed**

# Critical Challenges for Integrated Systems Nanomanufacturing

- **Control the assembly of three-dimensional heterogeneous systems**
- **Process nanoscale structures in high-rate/high-volume applications without compromising their inherent properties**
- **Ensure the long-term reliability of nanostructures through testing and metrics.**

# Emphasis for Future Needs of Systems Nanomanufacturing

- **Understand the mechanisms and patterns of integrated system behavior as a function of components, interaction forces, and networks at the nanoscale**
- **Consider the scalability of systems having large numbers of nanocomponents and non-linear interactions**
- **Establish reliable, reproducible and economically viable means of assembling arrays of nanoscale components, effectuating their deterministic placement and integrating the nanostructures with device architectures that span multiple length scales.**
- **Specific to manufacturing platforms ranging from wafer based batch processing to high speed, low cost roll-roll manufacturing platforms.**
- **Determine the tools required for measuring, simulating, and manufacturing of engineered nanosystems**
- **Establish the framework for product lifecycle and environmental health and safety controls addressing emerging functions of integrated nanosystems.**

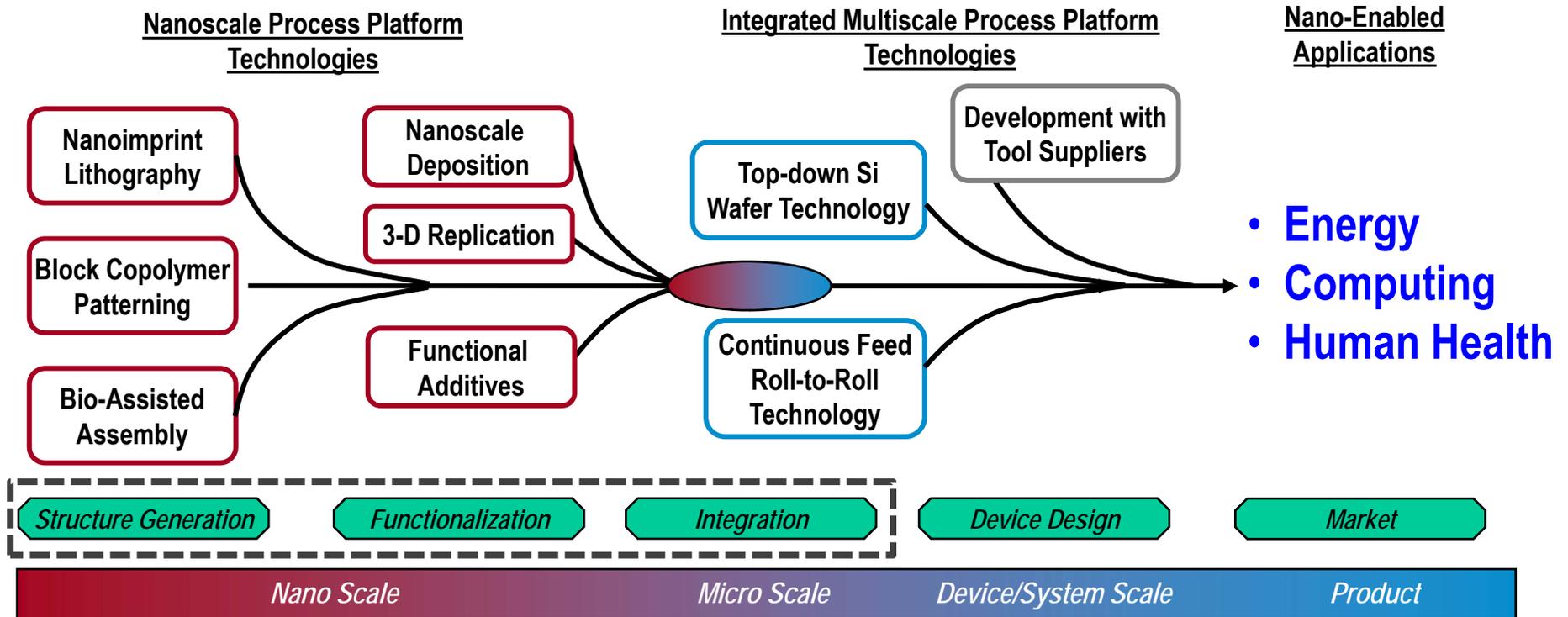
# NMS Workshop Format and Sessions

- **Integrated Nanomanufacturing Processes**
- **Manufacturing of Nanoscale Materials**
- **Metrology for Nanomanufacturing**
- **Breakout Session I: Integration for Nanosystems Manufacturing**
  - Target Applications
  - Challenges for Achieving Targets
  - Process Innovation and Needs
  - Tool Challenges
  - Training and Education Needs
  - Infrastructure and Fundamental Studies
- **Breakout Session II: Control, Design, and Metrology for Nanosystems**
  - Interaction of Control, Functionality, and Design of Nanosystems
  - Reliable Systems from Unreliable Components
  - Embedded Metrology for *in situ* Quality Control
  - Sensors and Actuation

## Workshop Conclusions: Need for Follow-on Research

- **Model systems to study nanoscale interactions and systems mechanisms.**
- **Understanding and exploitation of surface interactions.**
- **New nanoscale architectures enabling improved performance, new functionality, and integrated functionality.**
- **Robust integration and interfacing in order to maintain the properties of individual nanocomponents ruined by integration within scaled processes.**
- **Low cost, high rate systems for self-assembly including 3-D structures and deterministic placement of nanostructures, particularly on roll-roll platforms**
- **Design, model and simulation incorporating mechanistic, multi-scale methods supported by experimental validations.**
- **Embedded metrology, sensors and analysis techniques to better understand process performance at each step, provide details of the individual nanocomponent performance by observing macroscale properties of the system.**

# CHM Nanofabrication Research Platform



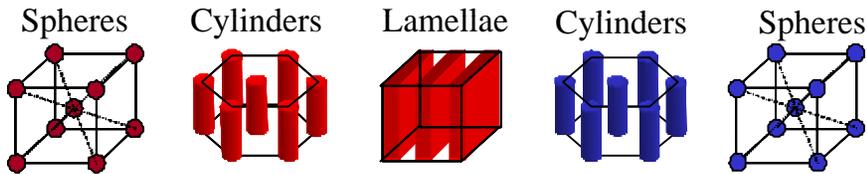
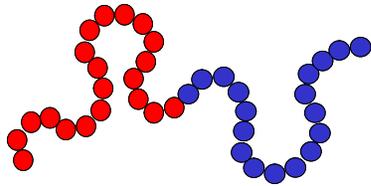
**Partners:** Univ. of Puerto Rico - Rio Piedras • Mt. Holyoke College • Springfield Technical Community College • Binghamton University • UC Riverside • TIAX LLC • Alcatel-Lucent

# A Few Enabling Advances in Self Assembly within the CHM

- Near Perfect Order Guided by Imperfect Surfaces
  - imprinting nanoscale texture on polymers with simple masters
- Well-Ordered Templates from Disordered Commodity Materials
  - blends of surfactants and homopolymers mimic block copolymer assembly
- Additive-Induced Assembly
  - improving order in polymer-nanoparticle hybrid materials using strong interactions
- Realization of Well Ordered 3 nm Domains

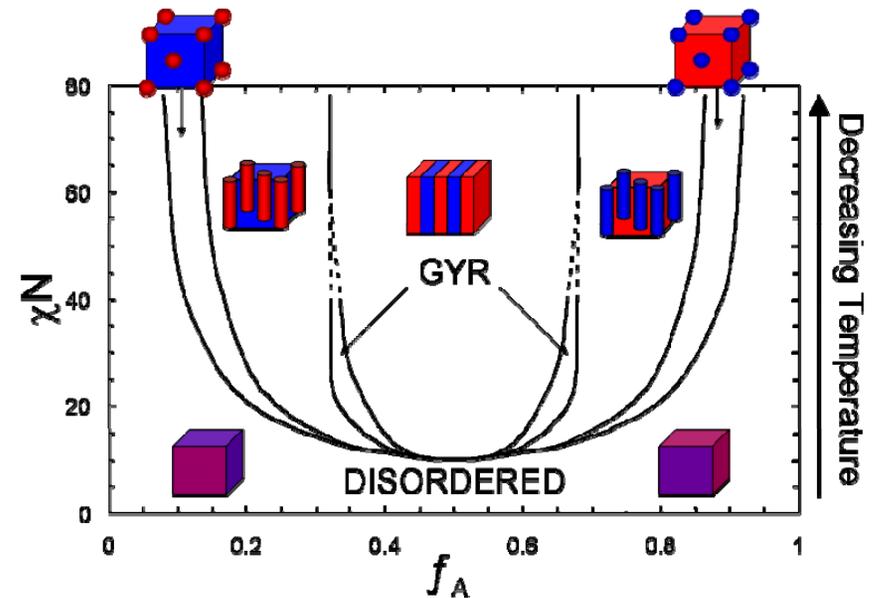
# Block Copolymer Templates: Spontaneous Assembly upon Spin Coating, Complete Control of Morphology

## Di-block Copolymer



Increasing  $f$   $\longrightarrow$

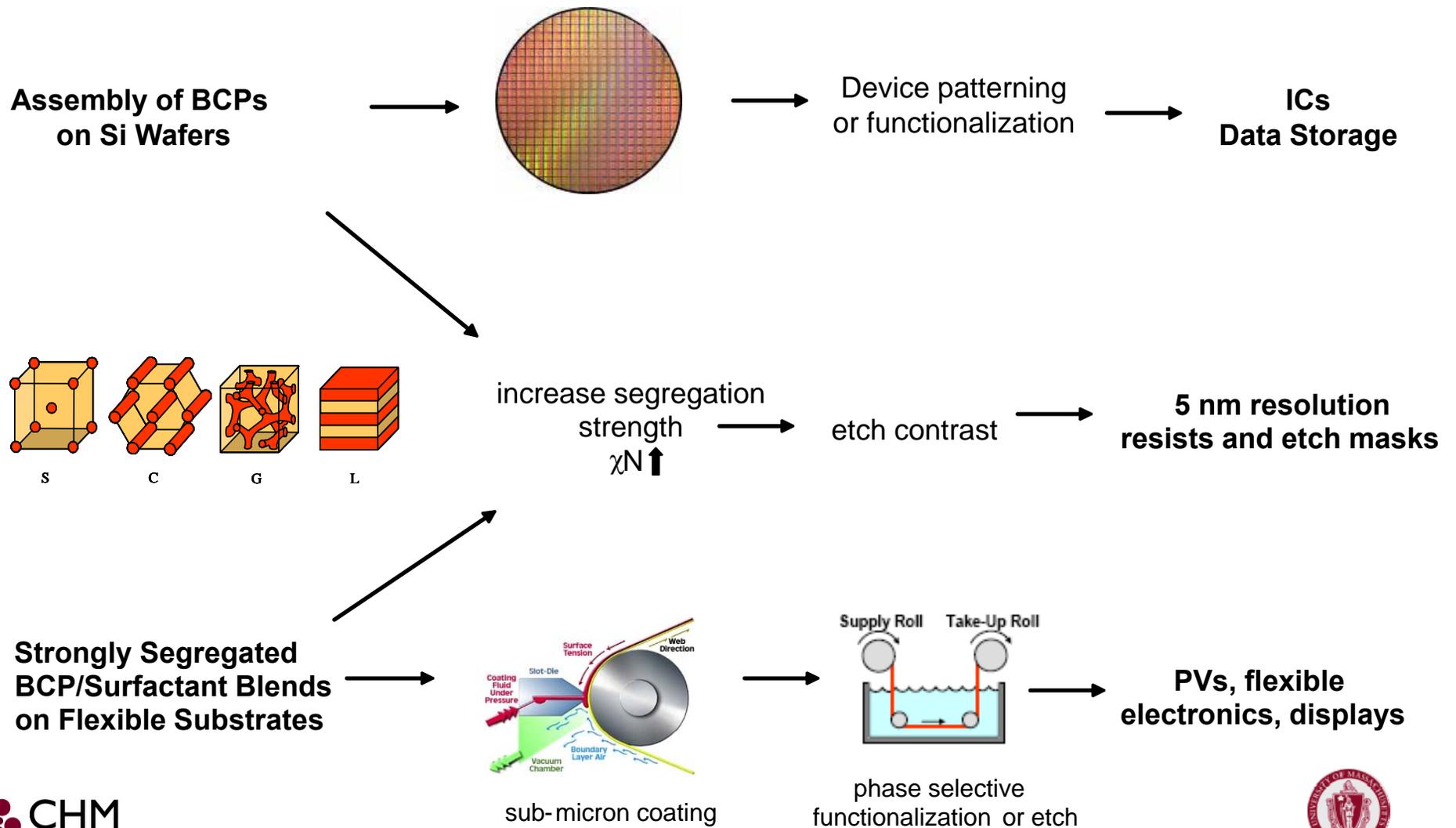
## BCP Phase Diagram



(Adapted from Bates, 1994; Matsen, 1996)

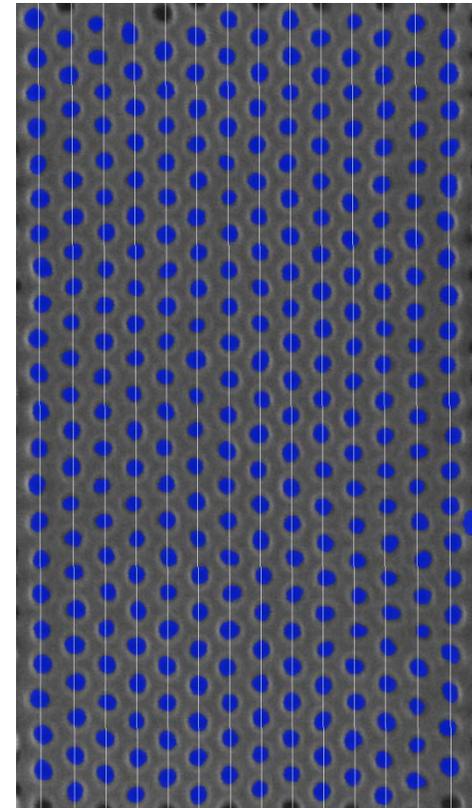
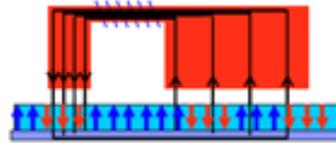
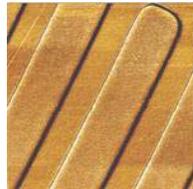
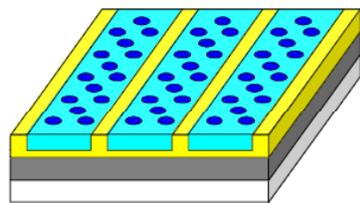
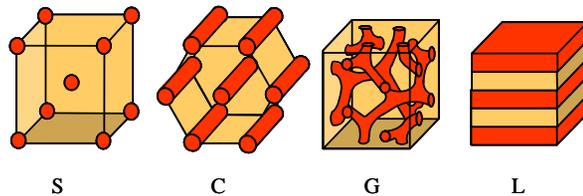
Key Parameters: block volume fraction,  $f \rightarrow$  controls morphology  
 Flory Parameter,  $\chi \rightarrow \chi N$  controls segregation  
 degree of polymerization,  $N \rightarrow$  controls domain size  
 small  $N$  requires large  $\chi$  for strong segregation

# Self-Assembled Templates for Device Applications: 2 Process Platforms



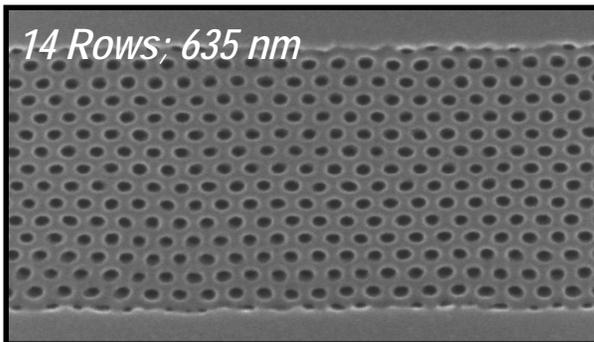
# Exploiting Cooperativity Across Length Scales: Hierarchical Processing Using Block Copolymers

## Evaluation of self assembly for ordered magnetic media



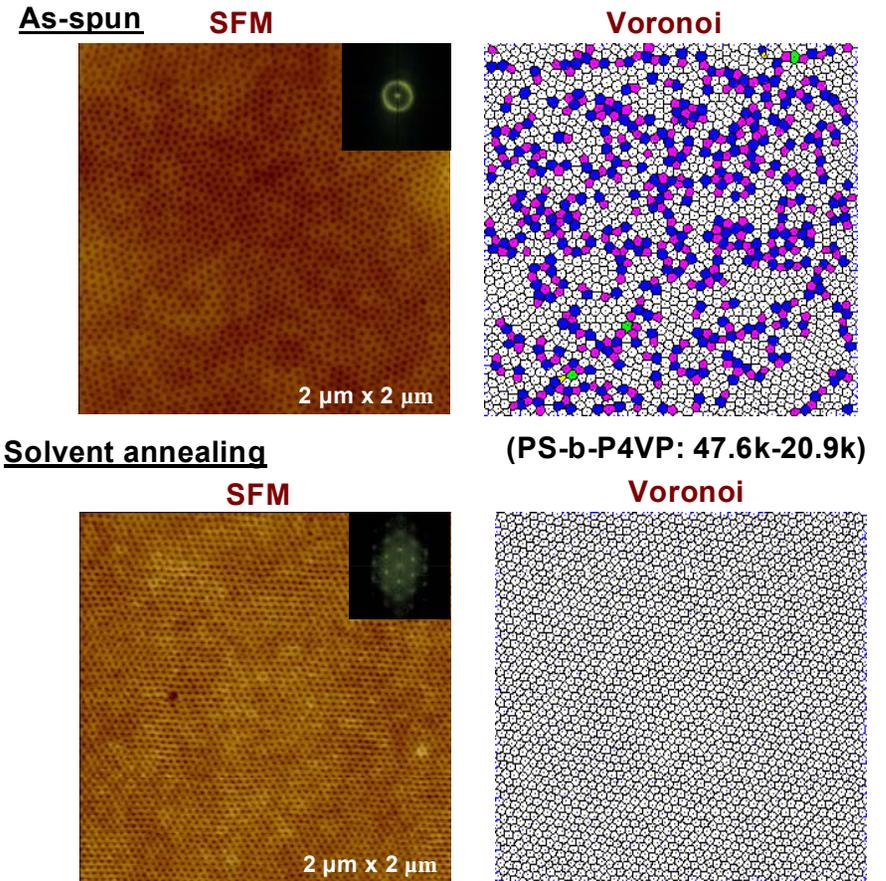
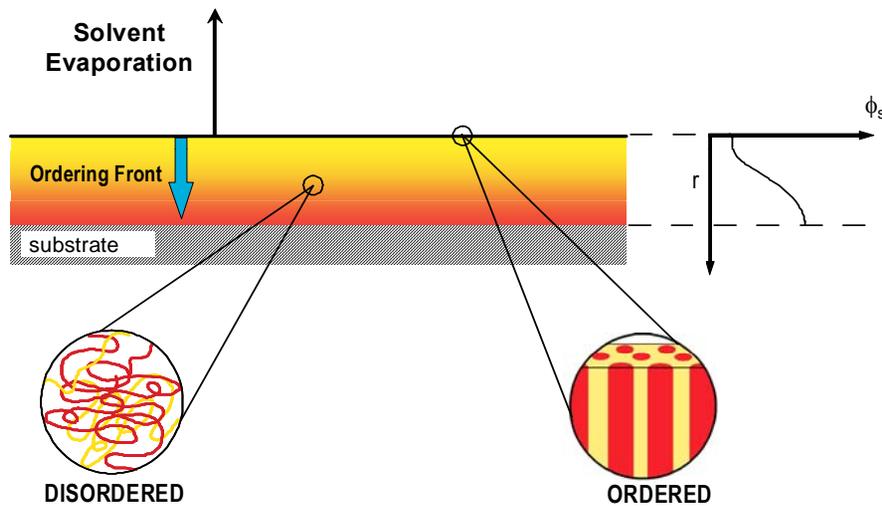
400 nm

Current requirement for magnetic data dots for BPM:  
Size and position distributions <5% per data sector



**Block Copolymers: Jitter of 4.5% !!**  
*With Oleg Myrasov Seagate Technologies*

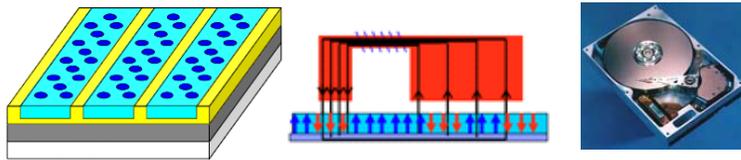
# Recent Progress: Vertical Orientation Via “Zone Refinement” and Near Perfect Lateral Ordering Through Solvent Annealing



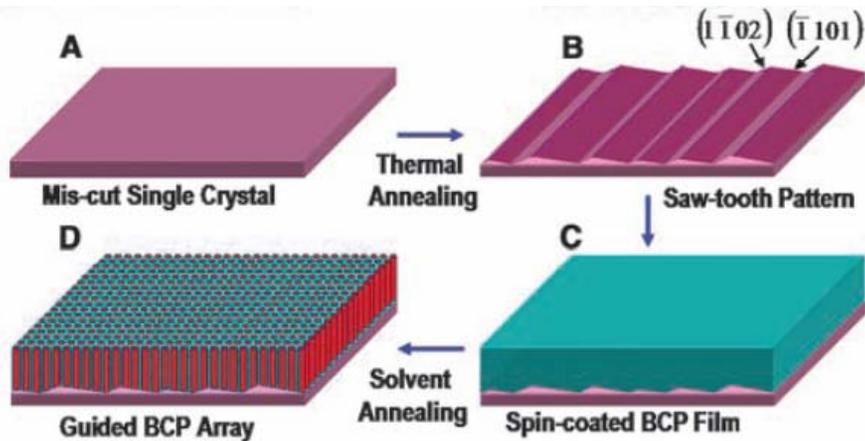
Work of Tom Russell at UMass

# Block Copolymers Templates as Etch Masks for Precision Electronics

## Ordered Magnetic Media Russell - UMass



M-plane (“sawtooth”) sapphire substrate



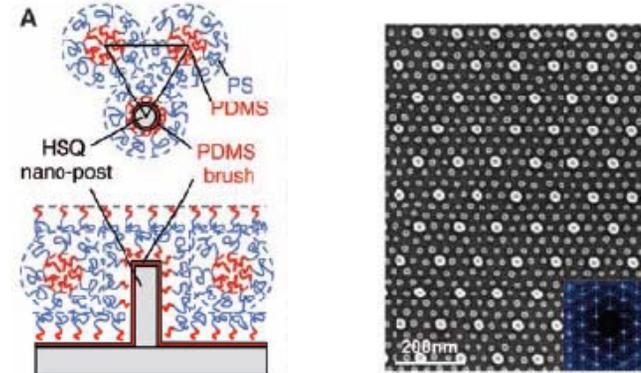
Ordered ~ 3 nm domains

(Science 2009)

## Ross, Thomas, Berggren - MIT

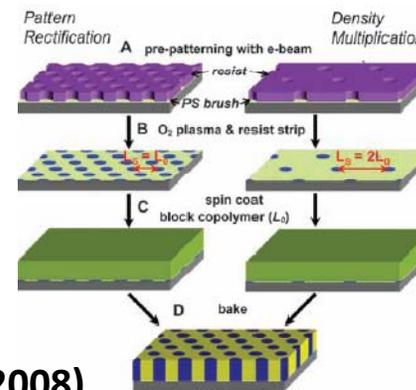
Graphoepitaxy – 20 nm spherical domains

(Science 2008)



## Albrecht, dePablo, Nealey - UW

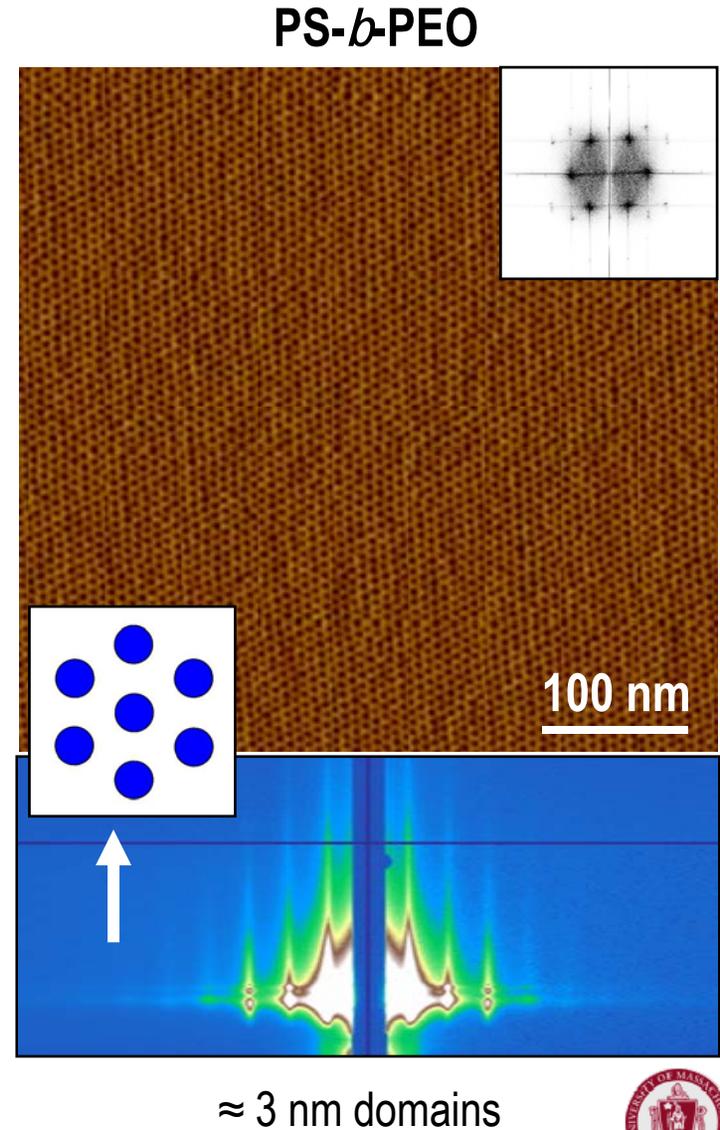
Density Multiplication - 15 nm spherical domains



(Science 2008)

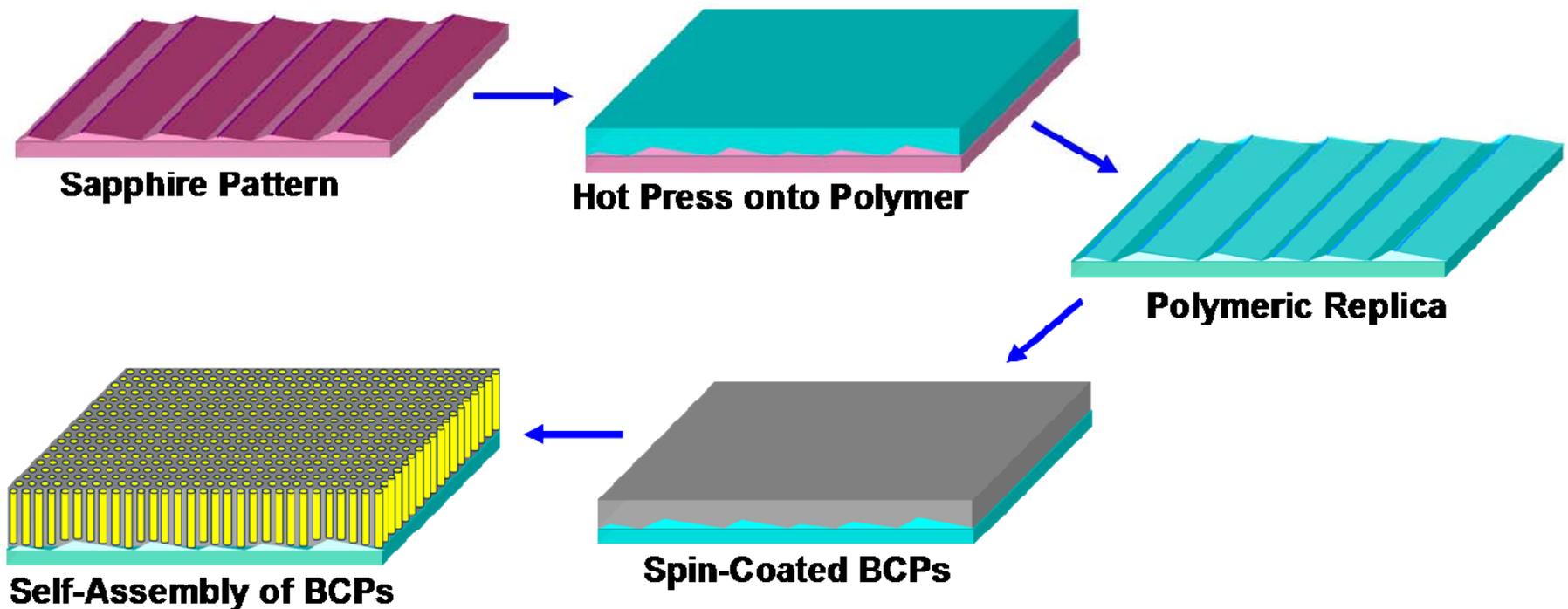
# Macroscopic 10 Terabit/in<sup>2</sup> Arrays from Block Copolymers

Atomic force micrograph of a BCP array with the corresponding a schematic and Fourier transform in the insets reflect the lateral order. GISAXS at bottom provides a nanoscopic to macroscopic metric.



T. P. Russell (UMass) and T. Xu (UC Berkeley)

# Pattern Replication Transfer Process



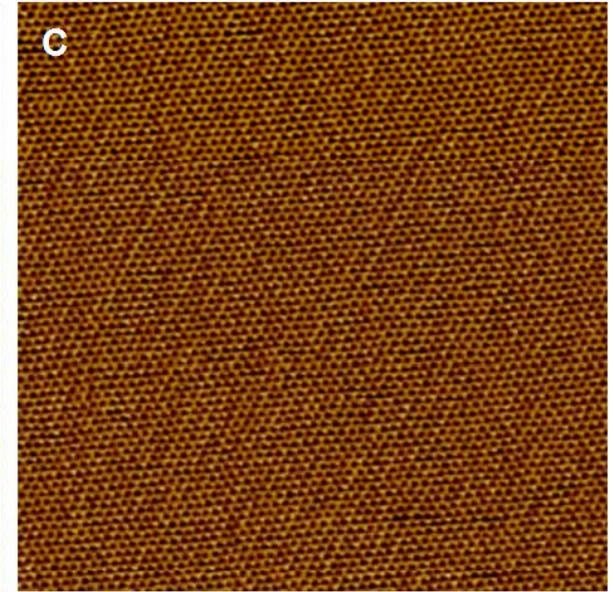
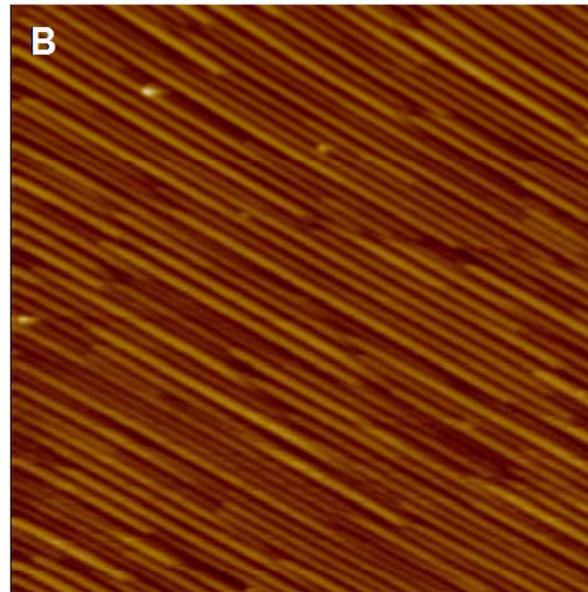
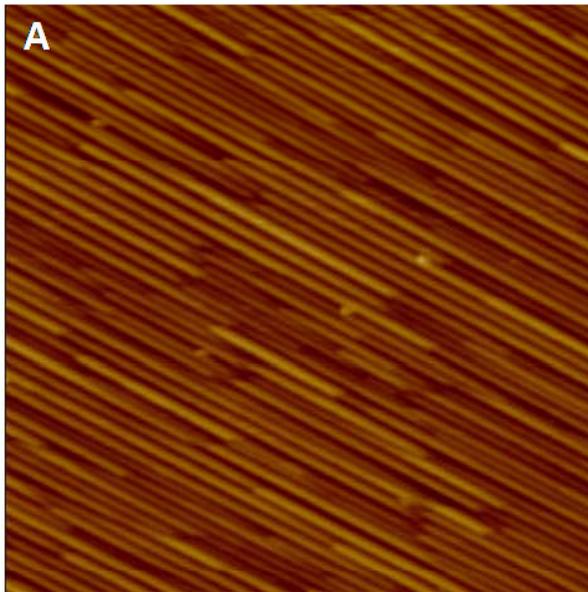
# BCP Ordering on Soft, Flexible Substrate

PS-*b*-PEO

Reconstructed Sapphire

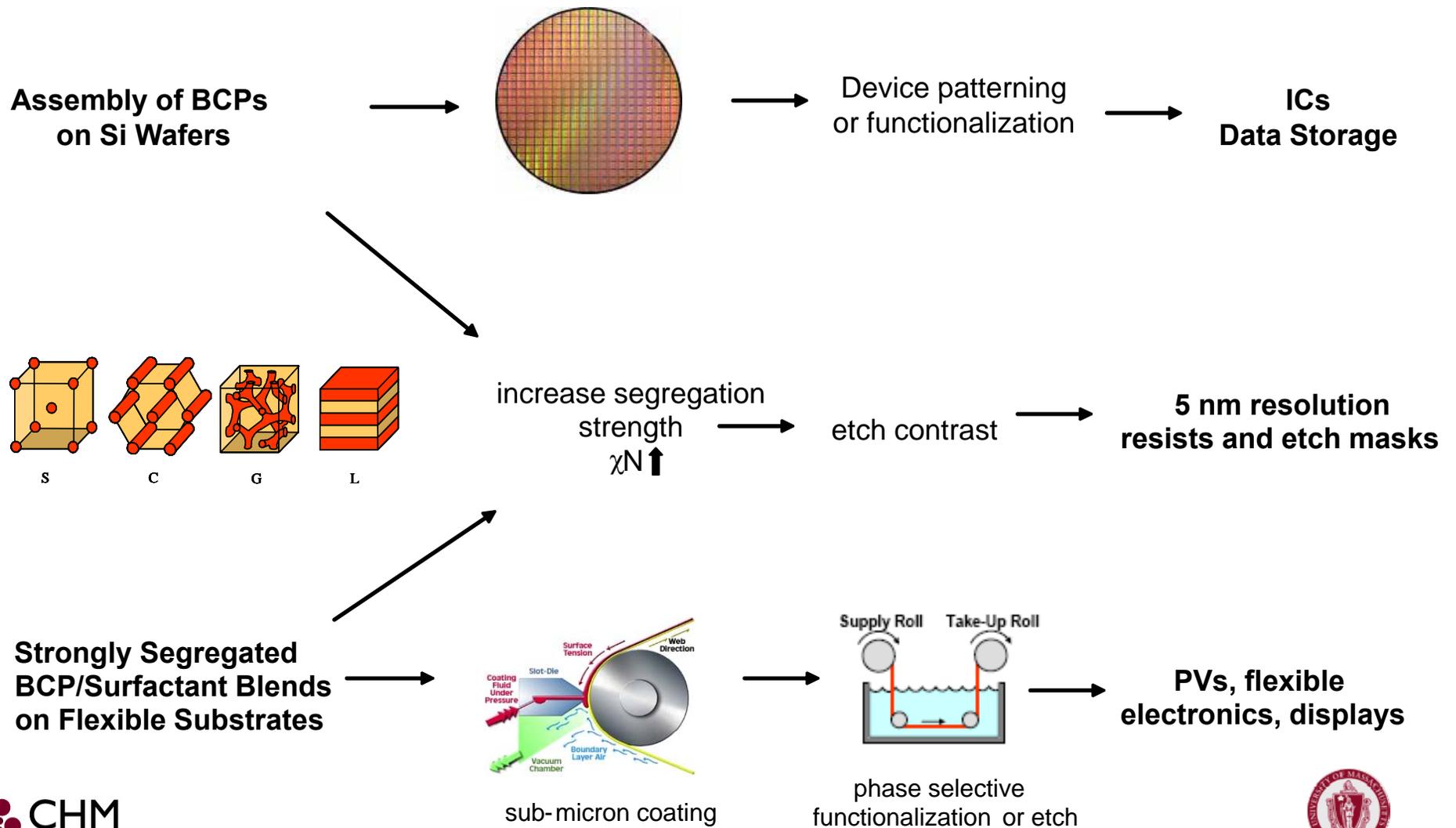
PBT Replica

Annealed in *o*-xylene vapor



2 um x 2 um

# Self-Assembled Templates for Device Applications: 2 Process Platforms



# Extension of Self-Assembly for High Volume Fabrication of Nanostructured Materials and Devices

- **Simple, rapid, cost-effective, process**
  - roll-to-roll
- **Commodity scale availability for low cost/high volume systems**
- **Increase strength of segregation to decrease feature size**
- **Creation of technologically useful materials: functionalize to realize electronic, mechanical, optical properties**
- **Overcome entropic penalties for ordering of NP/BCP systems**
- **Long-range ordering is necessary for some applications**
- **Real time metrology is difficult**

# Commodity Block Copolymers: Pluronic™ Surfactants

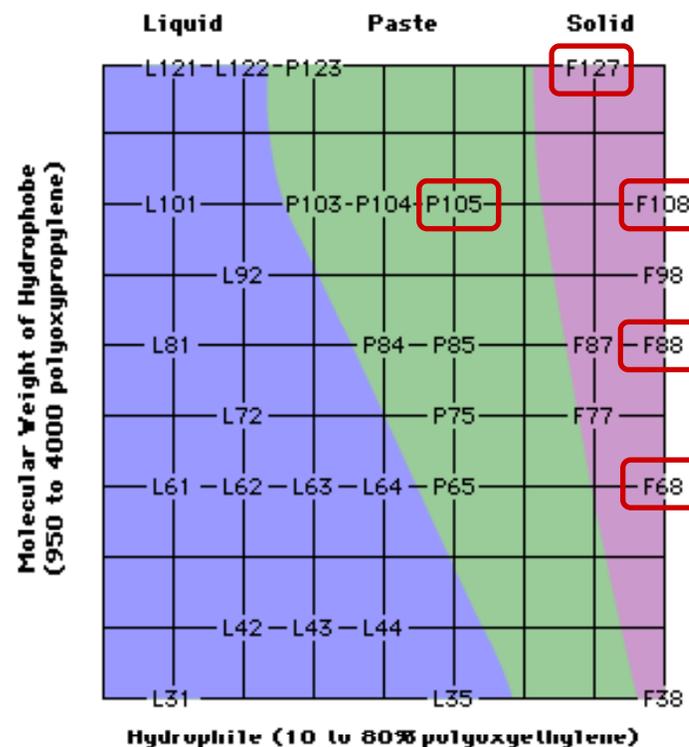
- PEO<sub>m</sub>-PPO<sub>n</sub>-PEO<sub>m</sub> (contaminated with diblock (Mw/Mn ~ 1.2))
- Inexpensive and readily available with various  $f_{PEO}$  and  $\Lambda$
- Low  $\chi_{PEO-PPO}$ :  $\chi(T) = -0.122 + 66.8/T^1$   
 $\chi_{PEO-PPO} @ 80^\circ C = 0.066 - 0.068$

## Segregation strength of Pluronics<sup>2</sup>

Polymer	Total M <sub>W</sub>	f <sub>PEO</sub>	$\chi N^*$ (calc.)	Min. ODT (K)*
L92	3,450	0.2	4.236	137
P123	6500	0.3	7.392	220
P105	6500	0.5	8.74	256
F108	14,600	0.8	20.29	337.5

\* Calculated for lamellae assuming low polydispersity and no impurities

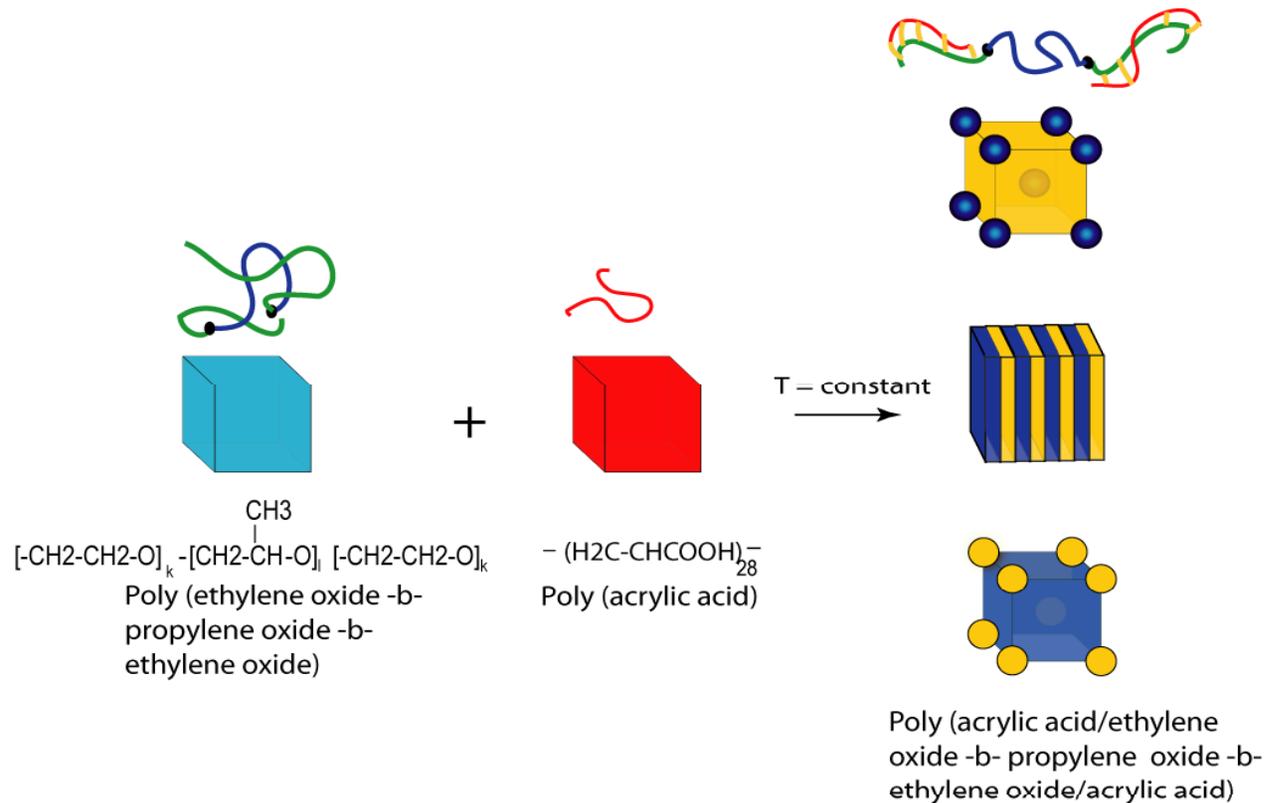
## Pluronics Grid



[http://www.basf.com/performancechemical/bcperfpluronic\\_grid.html](http://www.basf.com/performancechemical/bcperfpluronic_grid.html)

**No Microphase Separation at 80 °C**

# Well Ordered Polymer Melts from Blends of Disordered BCP Surfactants and Homopolymers



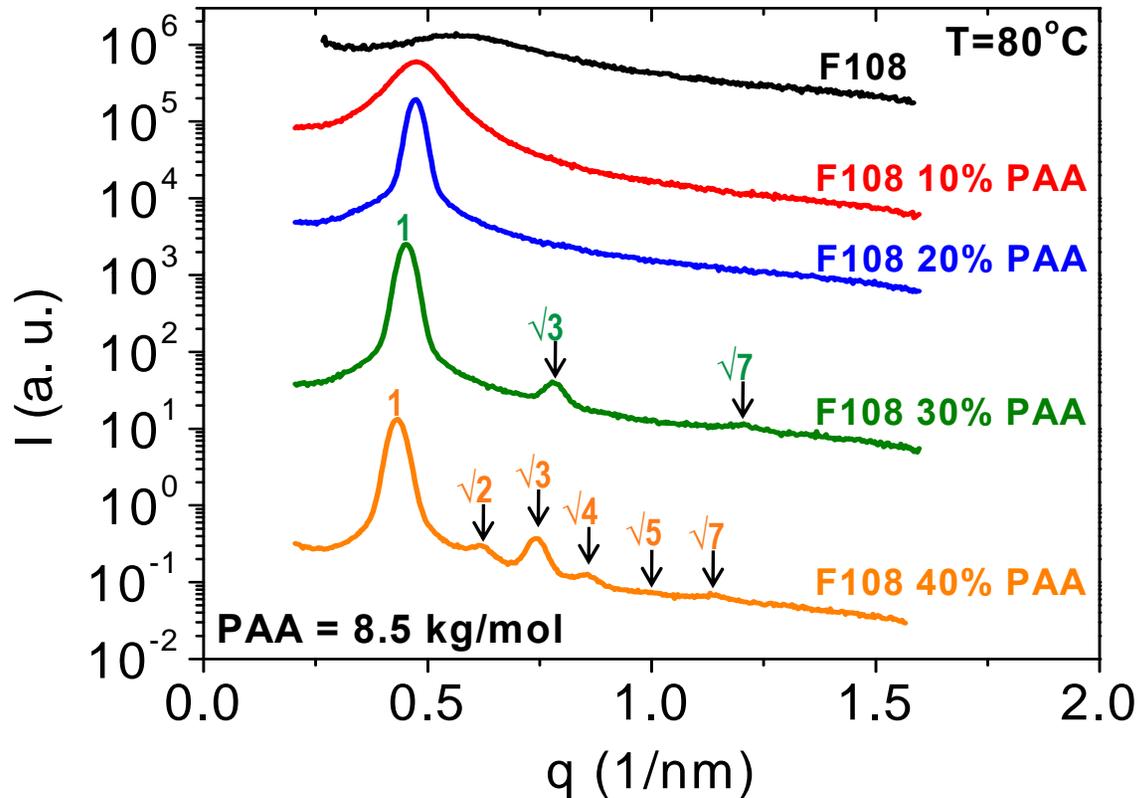
- Phase segregation maximizes number of PAA-PEO hydrogen bonds
- Repulsive PEO-PPO interactions increase with hydrogen bonding between

$$\chi_{CA-B} > \chi_{A-B} \text{ PEO/homopolymer:}$$

# Phase Transitions in Blends of F108 and PAA

F108 = (PEO<sub>127</sub>-PPO<sub>48</sub>-PEO<sub>127</sub>, 14.6 kg/mol)

PAA = 8.5 kg/mol

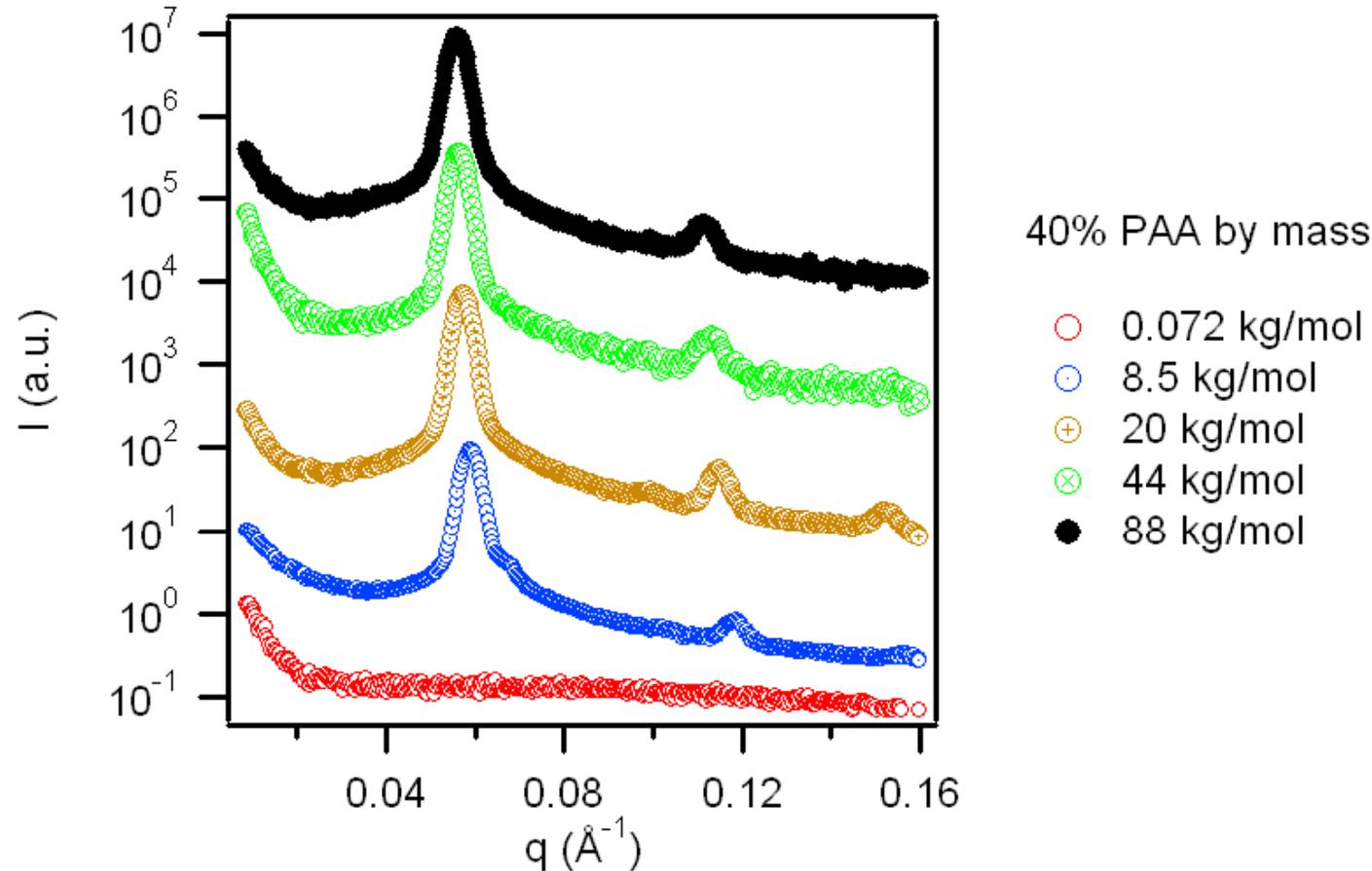


$d=13.9$  nm (at 30 % PAA)  
 $d=14.6$  nm (at 40 % PAA)

- Dramatically improved template order
- Increasing PAA: disordered  $\rightarrow$  cylindrical  $\rightarrow$  spherical morphology

# P105/PAA blends (40% PAA) : Influence of Homopolymer Mw

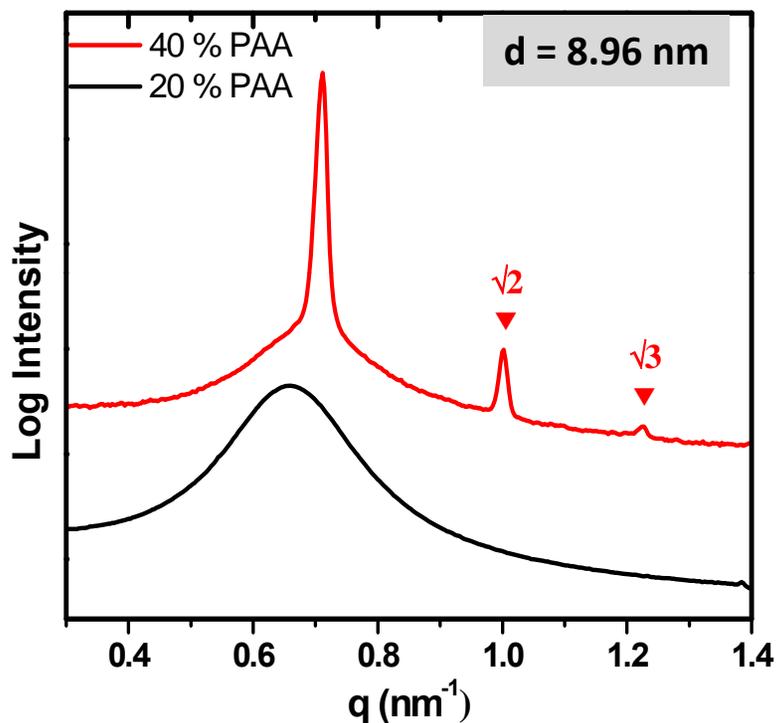
P105 = (PEO<sub>37</sub>-PPO<sub>56</sub>-PEO<sub>37</sub>); 6.5 kg/mol



- strong segregation over broad, but bounded, homopolymer Mw range
- 5 nm lamellar domains!

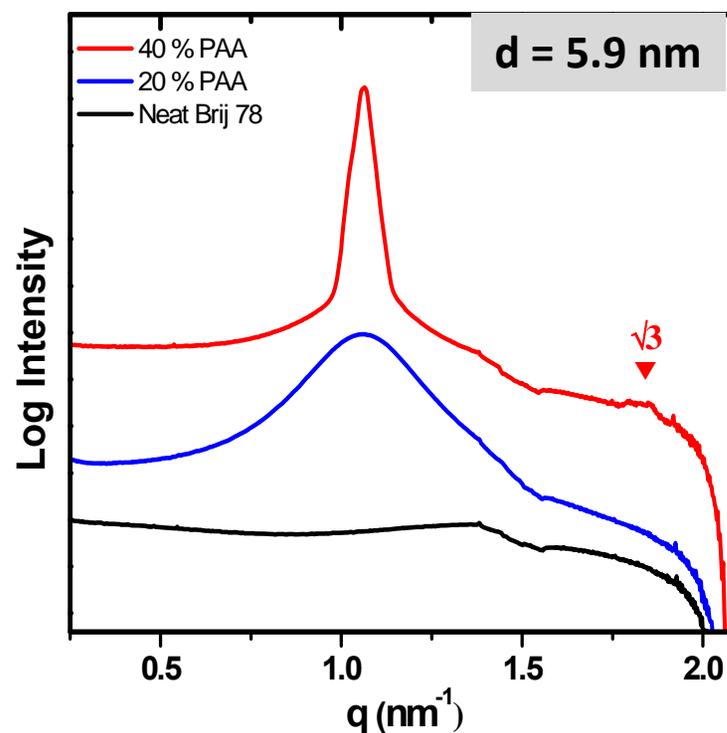
# Reducing the Domain Size with Low Mw Surfactants

F68 (PEO<sub>82</sub>-*b*-PPO<sub>31</sub>-*b*-PEO<sub>82</sub>) 70 °C



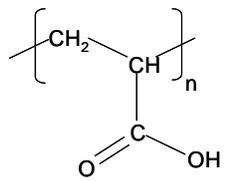
Disordered → **Spheres**

Brij 78 (PEO<sub>20</sub>-*b*-C<sub>18</sub>H<sub>27</sub>) 70 °C

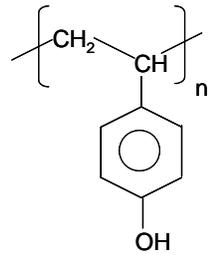


Disordered → **Cylinders**

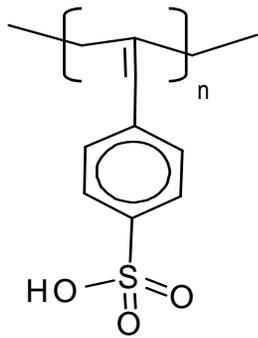
# Phase Segregation of Pluronic by Addition of Associating Homopolymers



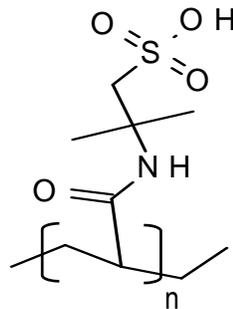
Poly(acrylic acid)



Poly(hydroxy styrene)

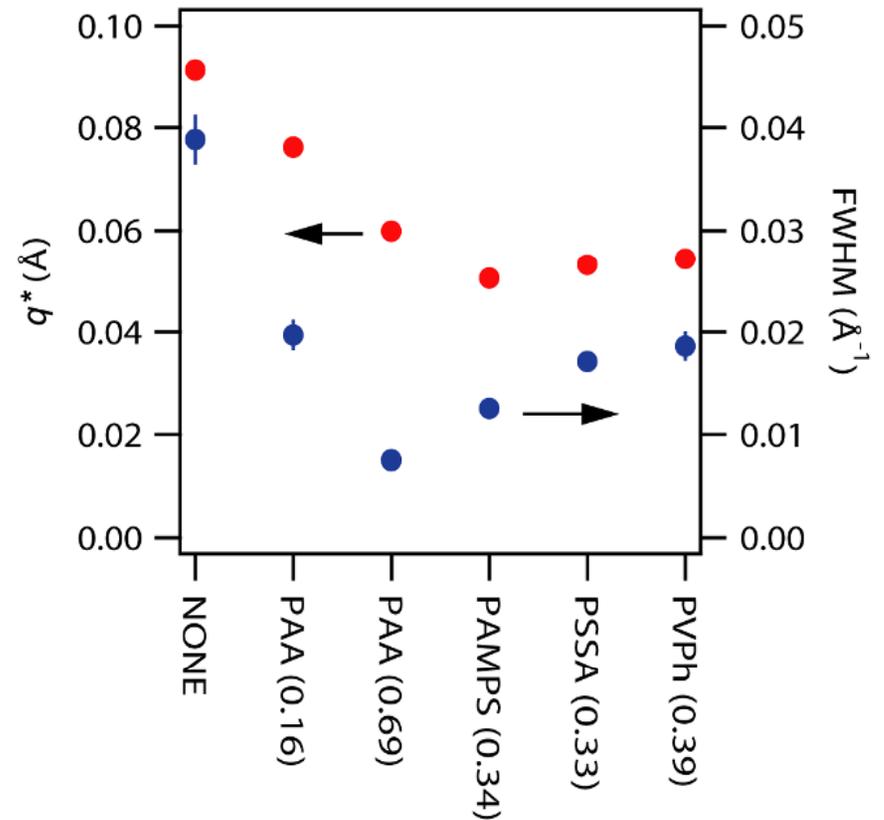


Poly (styrene sulfonic acid)



Poly (2-acrylamido,2-methyl, 1-propanesulfonic acid)

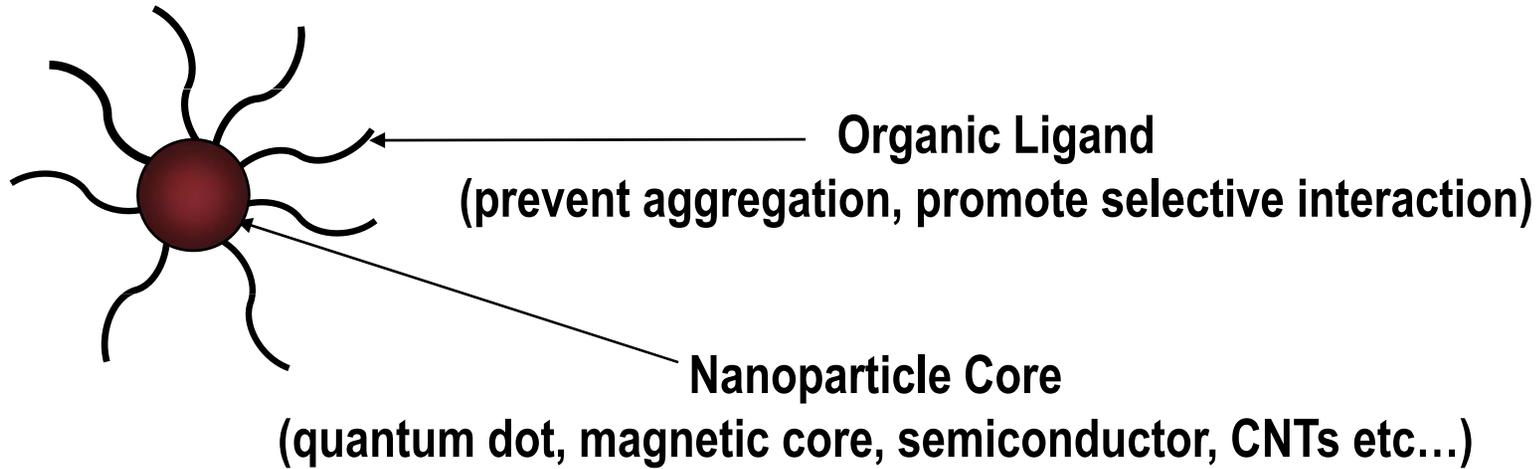
F68 (9 kg/mol) with 40% homopolymer loading



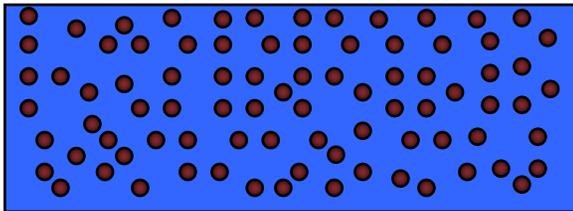
# Extension of Self-Assembly for High Volume Fabrication of Nanostructured Materials and Devices

- Simple, rapid, cost-effective, process
  - roll-to-roll
- Commodity scale availability for low cost/high volume systems
- Increase strength of segregation to decrease feature size
- Creation of technologically useful materials: functionalize to realize electronic, mechanical, optical properties
- Overcome entropic penalties for ordering of NP/BCP systems
- Long-range ordering is necessary for some applications
- Real time metrology is difficult

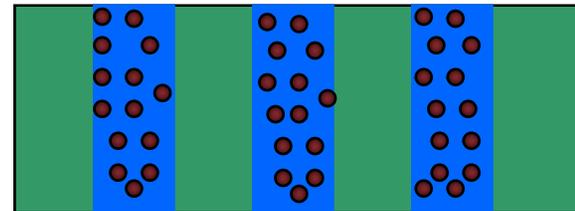
# Functional Polymer/Nanoparticle Hybrid Materials



**Homopolymers**  
*Uniform dispersion*



**Ordered Block Copolymers**  
*Selective dispersion*

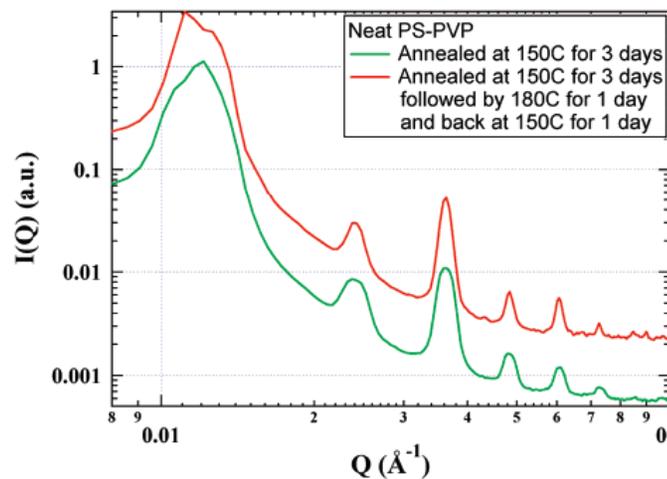


# Addition of NPs with Enthalpically Neutral Interaction Degrades BCP Order

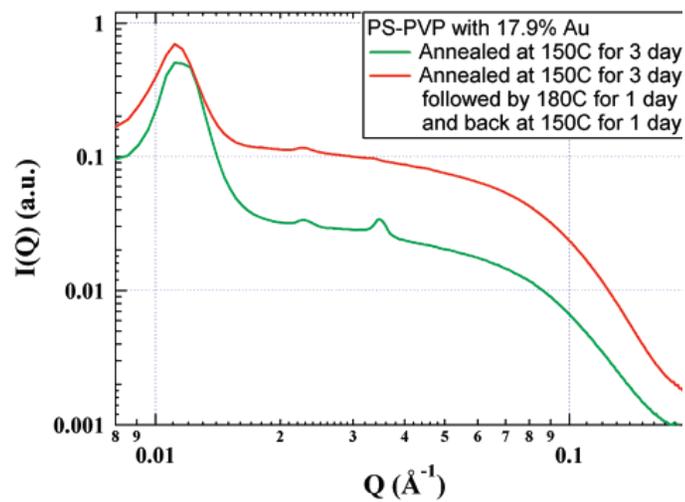
SAXS Study:

PS-*b*-PVP / Au-PS

*Lo et al., Macromolecules* **2007**, 40, 8302-8310



(a)



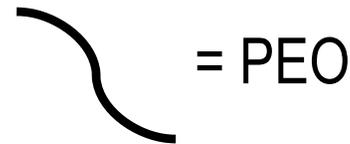
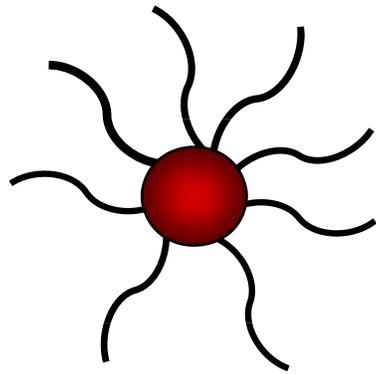
(b)

# Extension of Self-Assembly for High Volume Fabrication of Nanostructured Materials and Devices

- Simple, rapid, cost-effective, process
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- Long-range ordering is necessary for some applications
- Metrology

# Functionalized Nanoparticles in Ordered Surfactant Melts

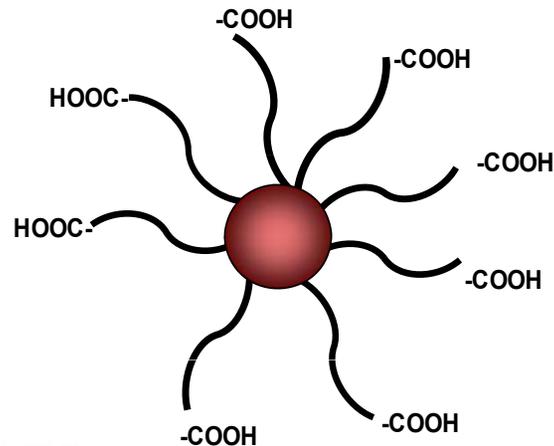
Can ligands be used to drive sequestration?



For example:

Ordered CdSe Nanoparticles within Self-Assembled Block Copolymer Domains on Surfaces  
Shan Zou, Rui Hong, Todd Emrick and Gilbert C. Walker, *Langmuir* 2007, 23

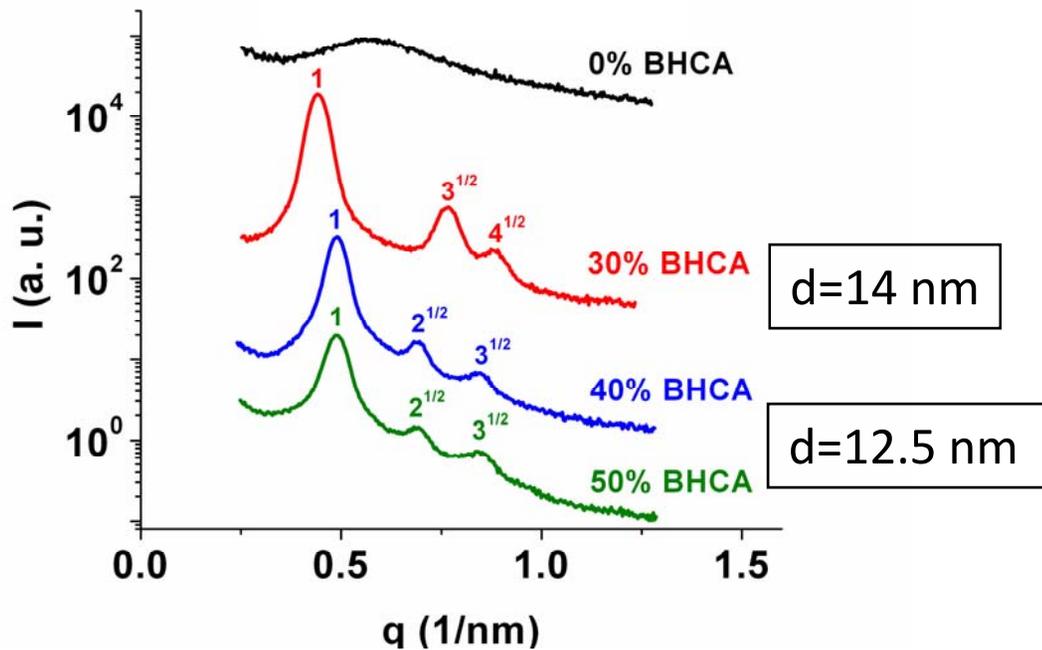
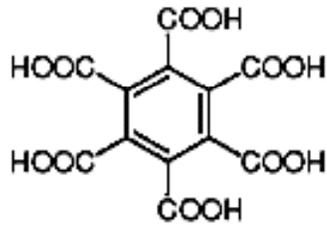
Can ligands be used to drive segregation + sequestration?



Completely or end  
functionalized ligands

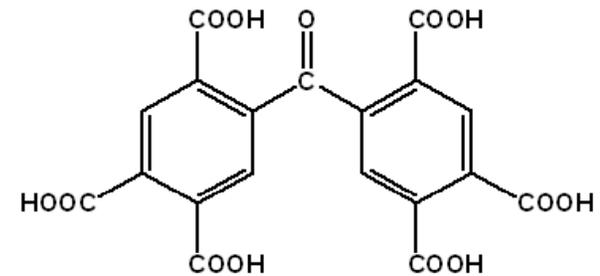
# Phase Behavior of F108 with Benzenehexacarboxylic Acid

## Benzenehexacarboxylic Acid (BHCA)

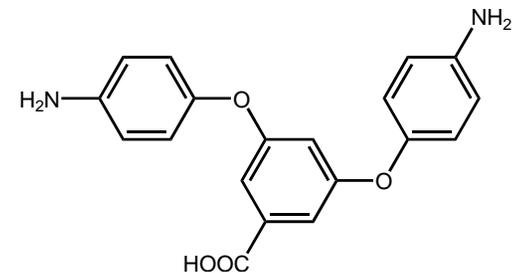


## Other additives...

### 5,5'-Carbonylbis-(trimellitic acid)



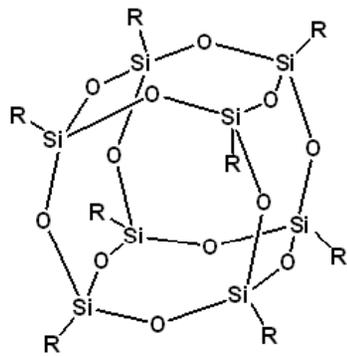
### 3,5-Bis(4-aminophenoxy) benzoic Acid



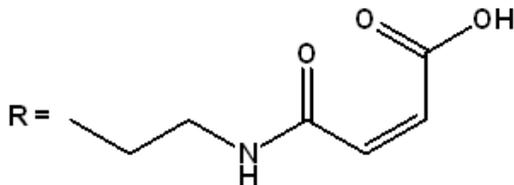
Phase segregation induced by BHCA  
disordered  $\rightarrow$  cylindrical  $\rightarrow$  spherical

# Self Assembly of Pluronic upon Blending POSS Octa Amic Acid

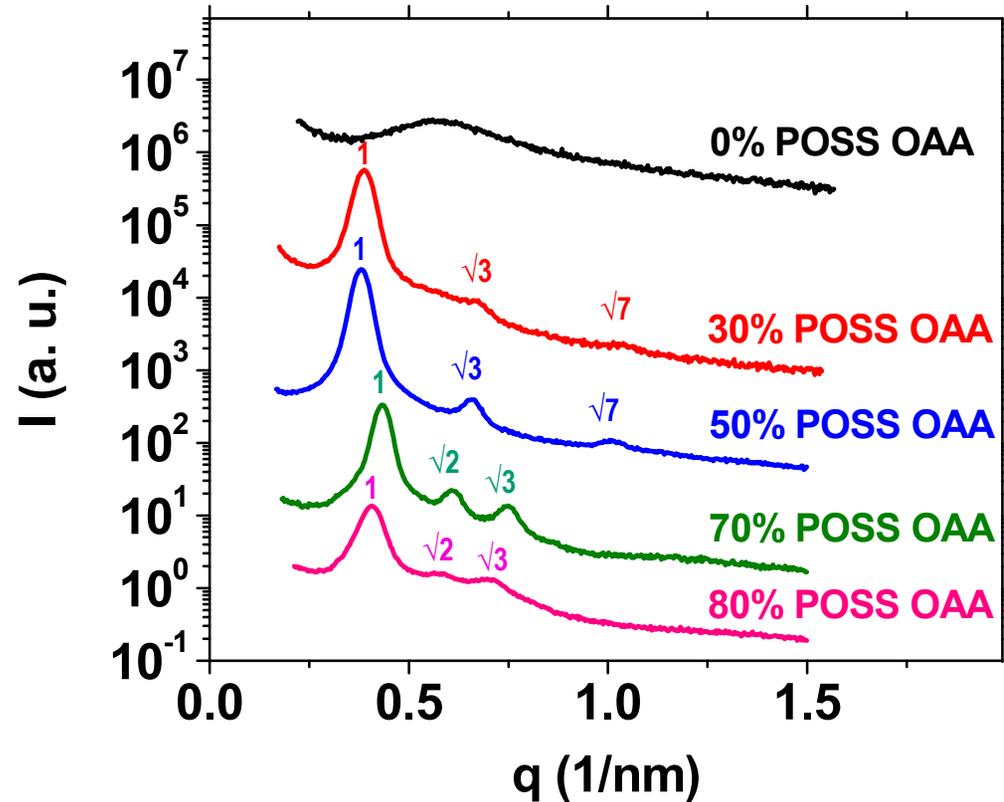
## POSS octa amic acid (POSS OAA)



$M_w = 1592$  g/mol  
Cage = 26 wt. %



## Pluronic=F108, T=80°C



- Multipoint hydrogen bonding interactions
- Ability to incorporate high concentrations of POSS without loss of morphology
- Applications as nanoscale etch resists

# Extension of Self-Assembly for High Volume Fabrication of Nanostructured Materials and Devices

- **Simple, rapid, cost-effective, process**
  - roll-to-roll
- **Commodity scale availability for low cost/high volume systems**
- **Increase strength of segregation to decrease feature size**
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- **Real time metrology is difficult**



# Conclusions

- Well ordered templates can be produced by the self-assembly of commodity materials
- Strong selective interactions with additives/nanoparticles can strengthen segregation and order in hybrid materials
- Imperfect surface textures can guide near perfect order
- Transfer of self-assembly to roll-to-roll processing is within reach
- On-line metrology is an issue

# Acknowledgments



**CHM**

Center for Hierarchical Manufacturing  
University of Massachusetts Amherst



Semiconductor  
Research Corporation



# Group 1: Process Yield and Repeatability

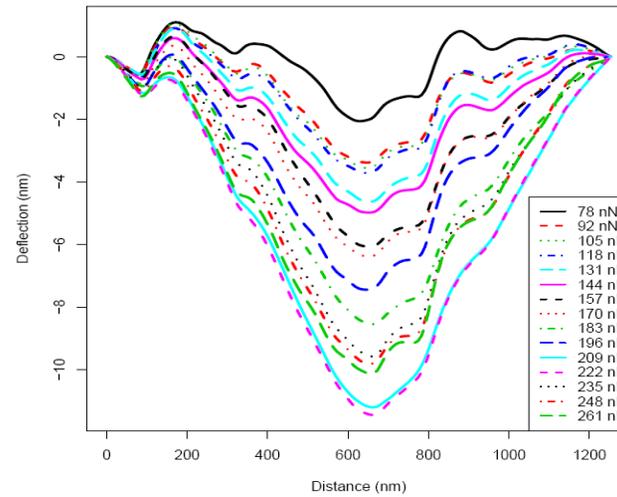
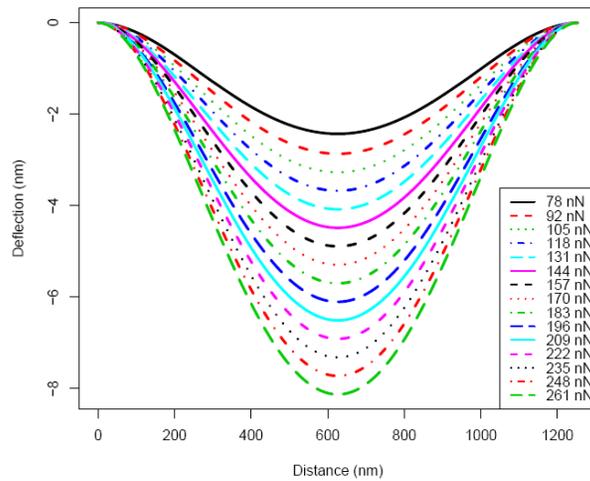
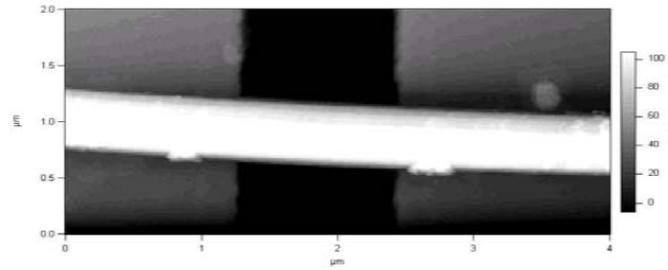
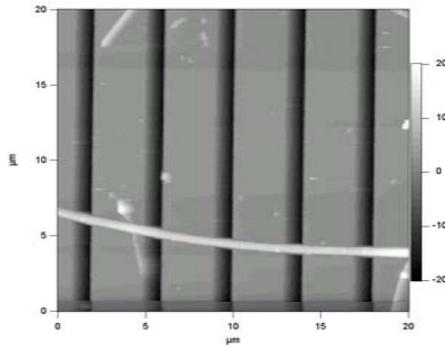
V. Roshan Joseph

**Acknowledgements:** Prof. Z. L. Wang, Dr. Jinhui Song,  
and Mr. Sheng Xu, Material Science and Engineering, Georgia Tech

# Challenges in nanomanufacturing

- The errors get magnified at the nanoscale (which could have been ignored in the conventional manufacturing).
  - More noise factors-> more problems.
- The physics of the manufacturing process is not well-understood compared to that in conventional manufacturing
  - More difficult to improve process

# An Example

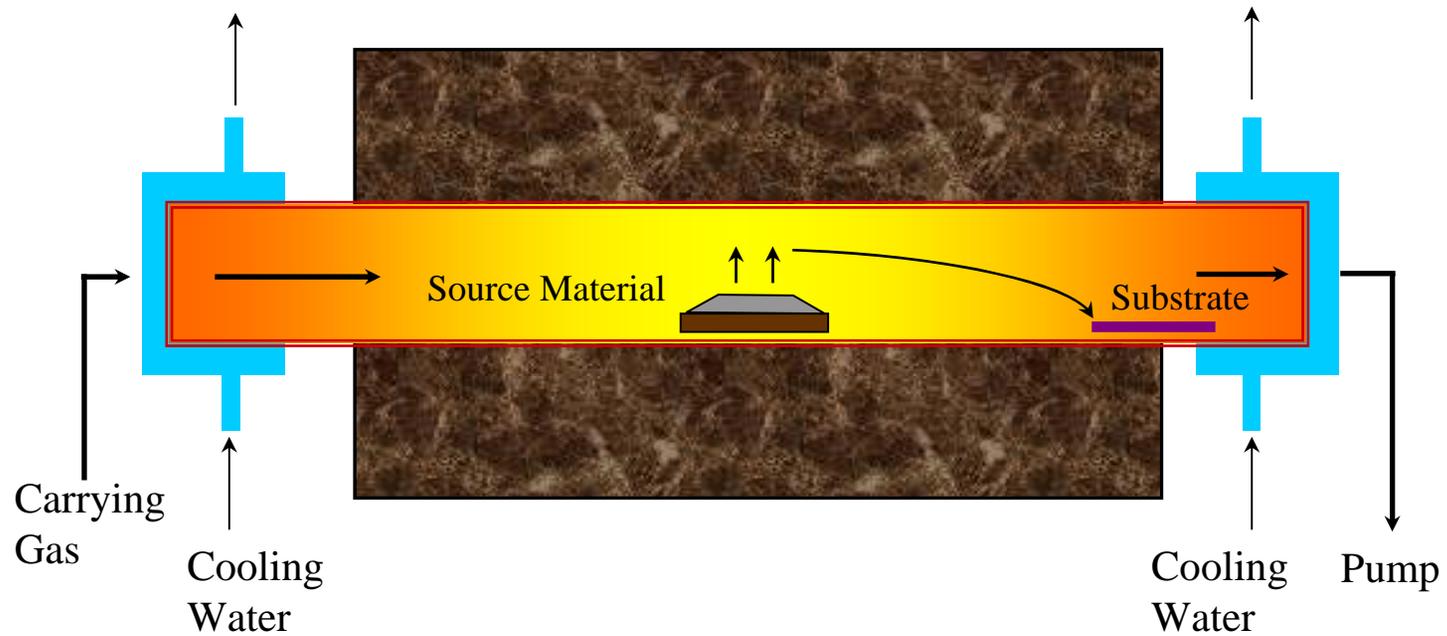


# Current Status

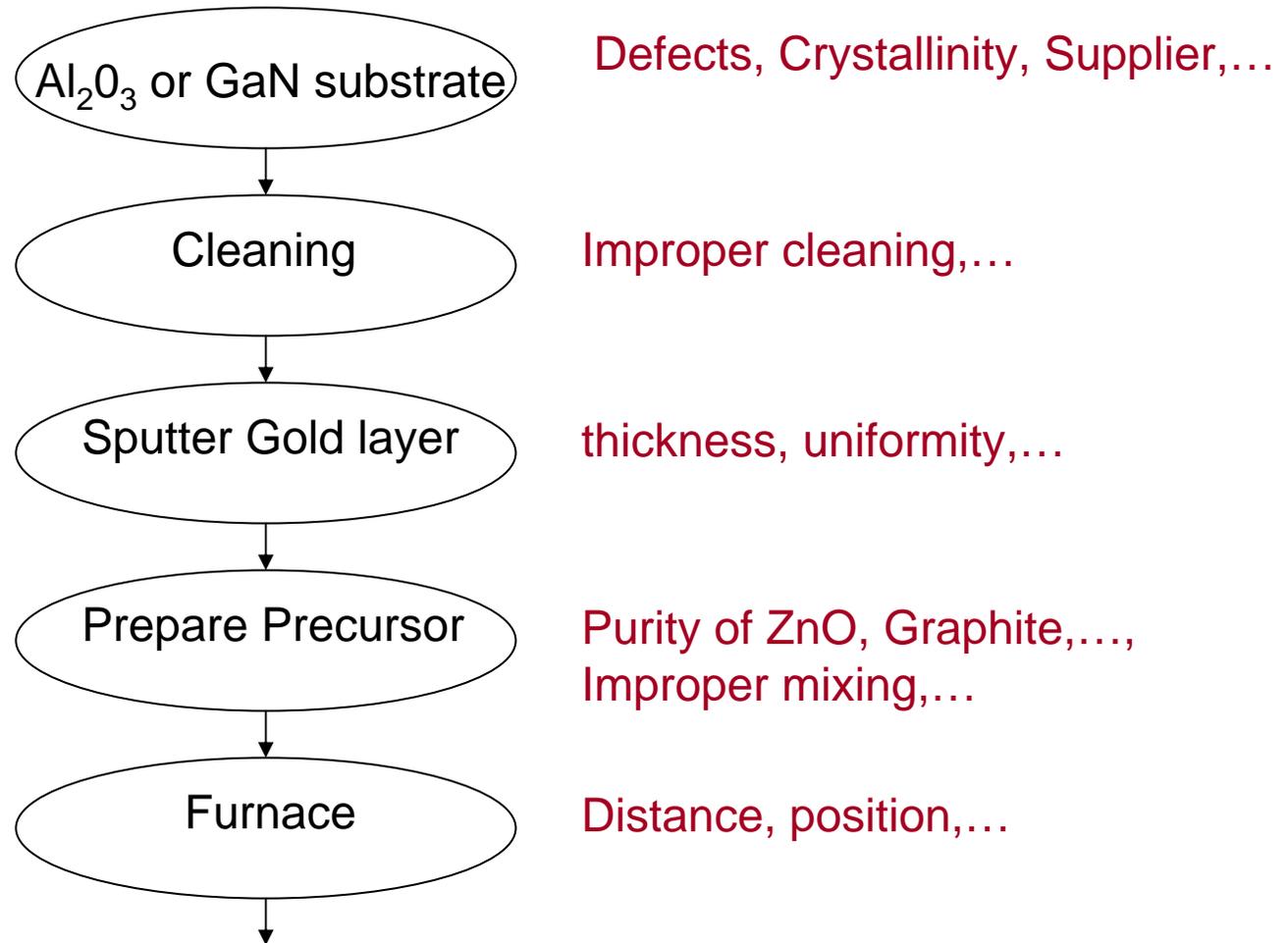
- Z. L. Wang's lab at Georgia Tech
  - Thermal Evaporation Process: Yield ~ 50% \*
  - Wet Chemical Process: Yield ~ 90% \*
- Yield can drastically go down in large-scale manufacturing.

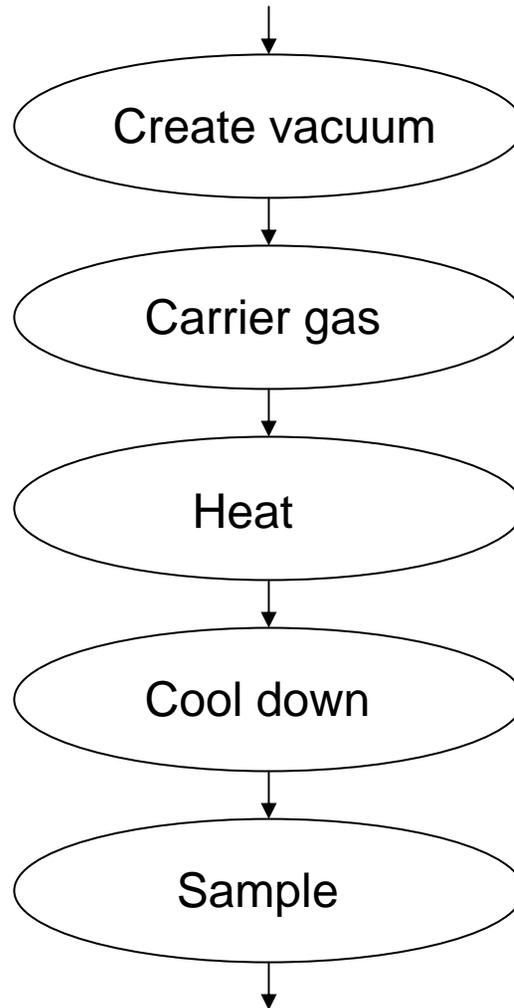
\*rough estimates

# Thermal Evaporation Process



# Possible Causes of Low Yield





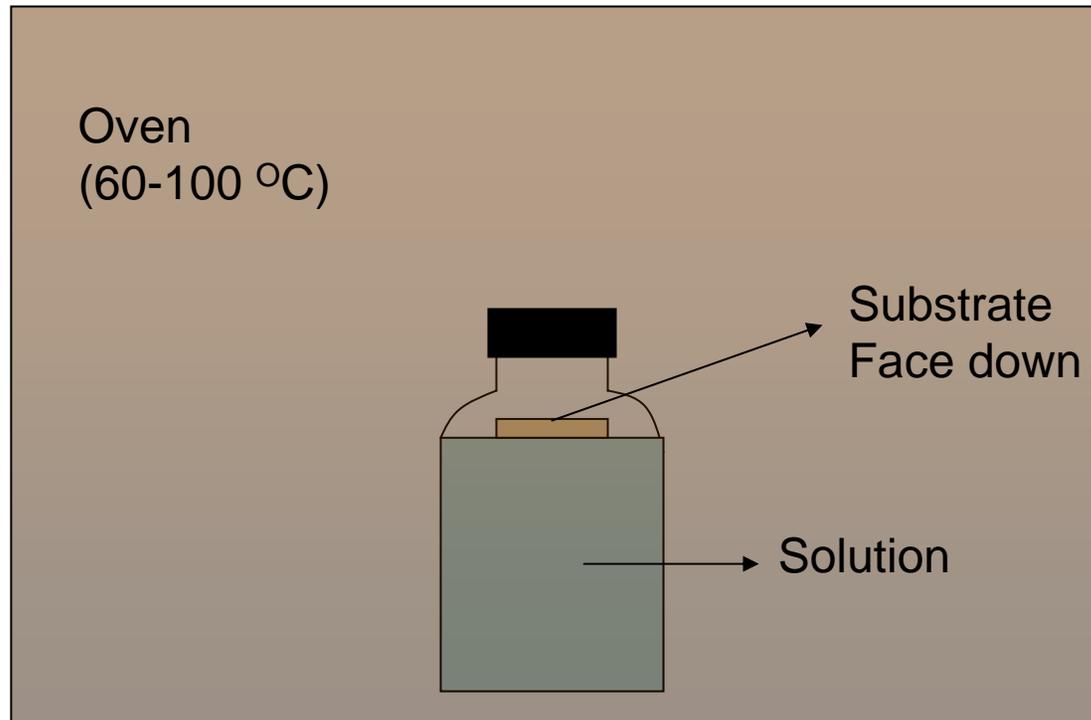
Leakage, pressure variation,...

Supplier, flow rate, impurities,  
Humidity,...

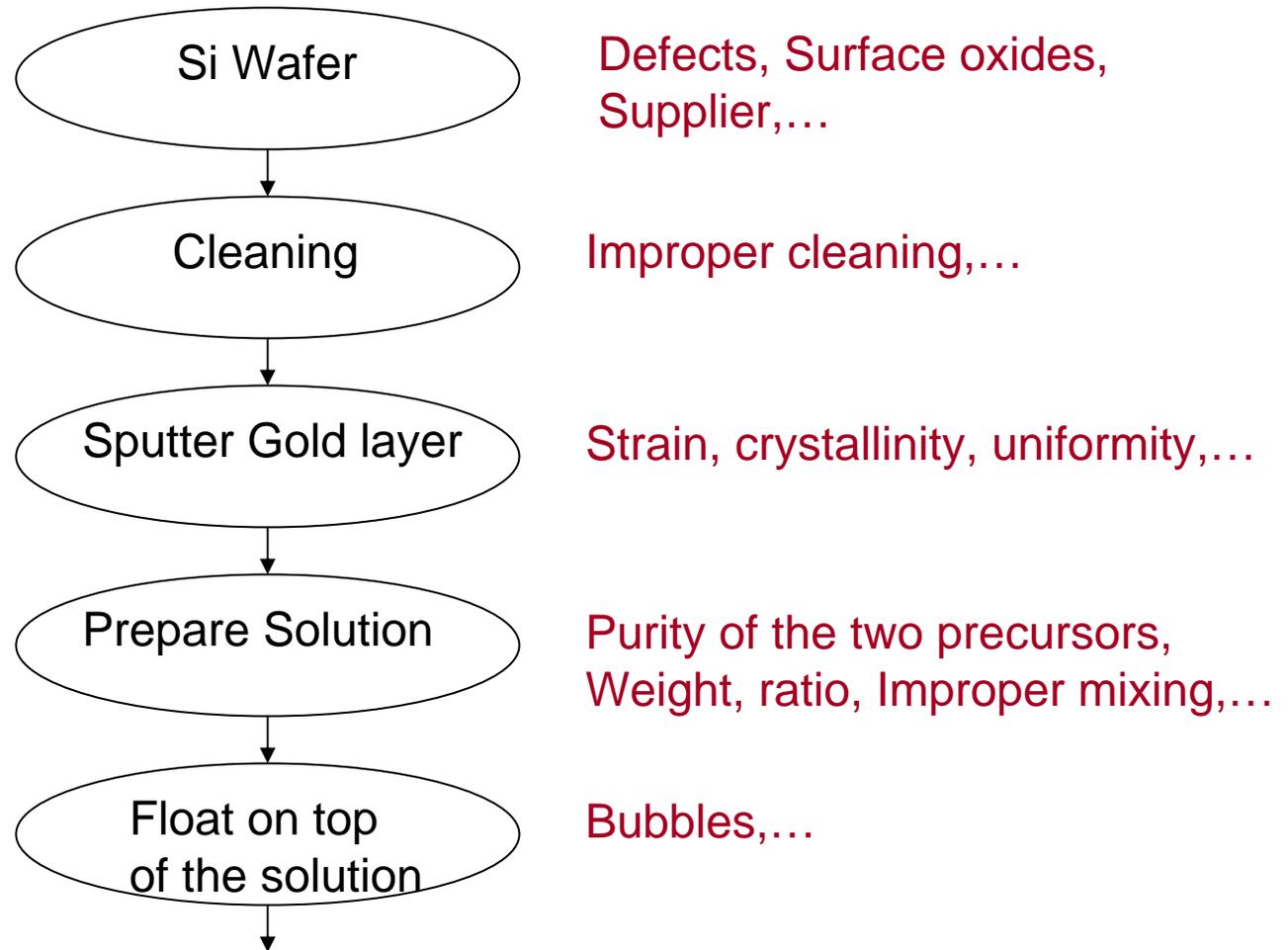
Furnace condition, temperature,  
Temperature distribution,...

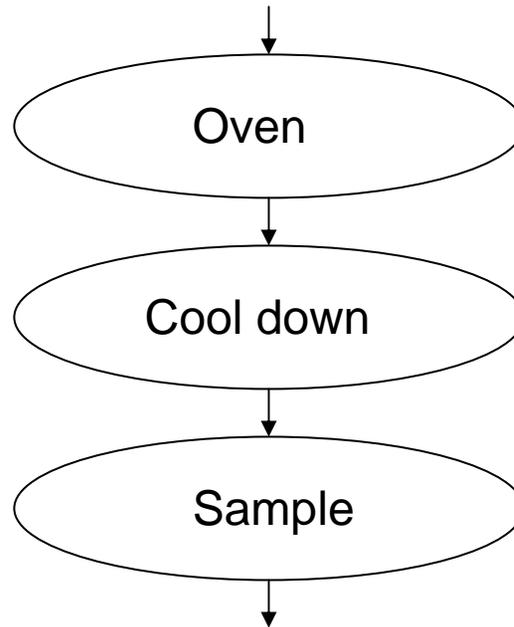
Rate of cooling,...

# Wet Chemical Synthesis



# Possible Causes of Low Yield





Temperature distribution,...

Room temperature, Humidity,  
Cooling rate,...

# Scale-Up

- More number of noise factors
  - Lower yield
  - Lower repeatability
- Possible causes
  - More number of furnaces and ovens
  - More number of people
  - “size effect”-> everything is larger

# Size Effect

Lab

Industry



More variations



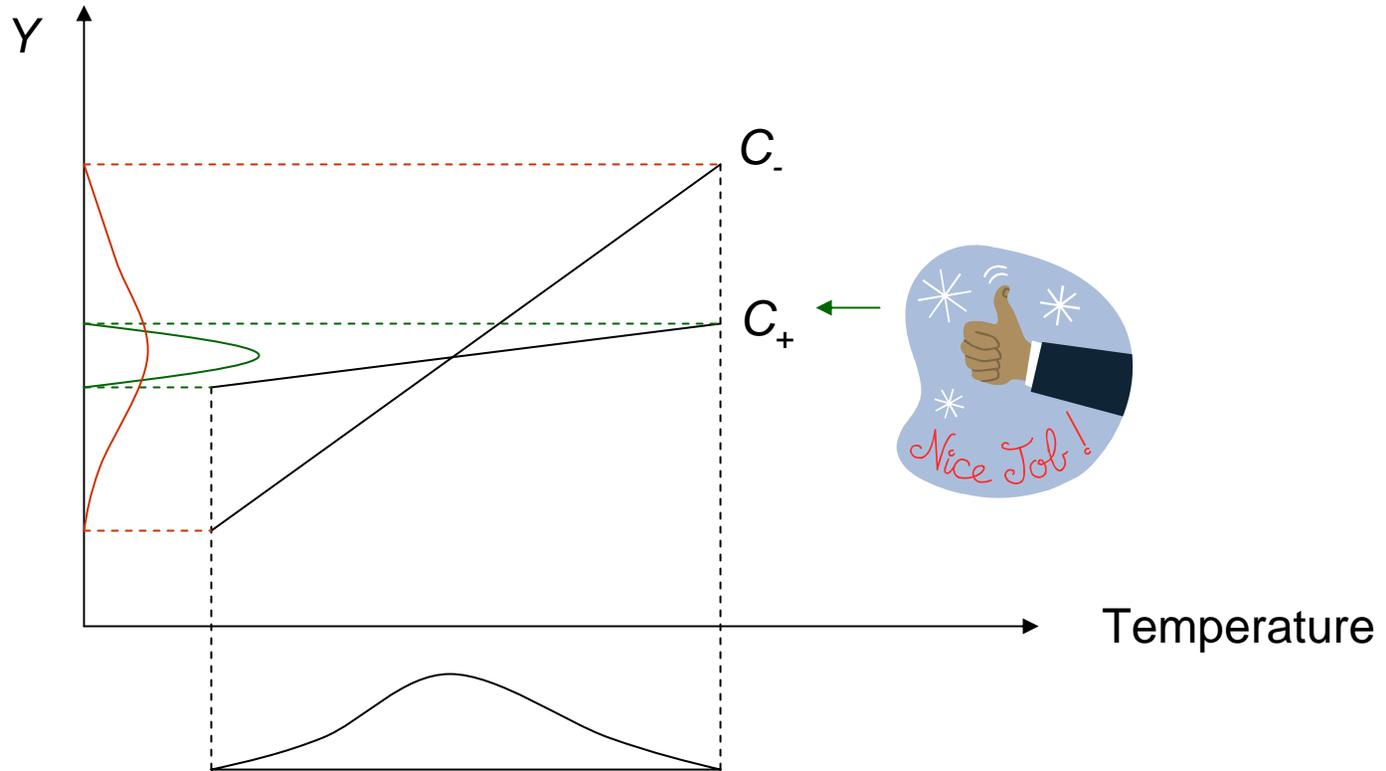
$950 \pm 10 \text{ } ^\circ\text{C}$

$950 \pm 20 \text{ } ^\circ\text{C}$

# Recommendations

- More number of furnaces/ovens
  - Calibration
- More number of people
  - Training
  - SOP
- “Size effect”
  - Better design, better control, robustness,...

# Robustness



- Robust parameter design (Taguchi)

# References

1. Dasgupta, T., Ma, C., V. Roshan Joseph, Wang, Z. L., and Wu, C. F. J. (2008). “Statistical Modeling and Analysis for Robust Synthesis of Nanostructures”. *Journal of the American Statistical Association* 103, 594-603.
2. Deng, X., V. Roshan Joseph, Mai, W., Wang, Z. L., and Wu, C. F. J. (2009). “A Statistical Approach to Quantifying Elastic Deformation of Nanomaterials”. *Proceedings of the National Academy of Sciences*, 106, 11845-11850.
3. Xu, S., Adiga, N., Ba, S., Dasgupta, T., Wu, C. F. J., and Wang, Z. L. (2009). “Optimizing and Improving the Growth Quality of ZnO Nanowire Arrays Guided by Statistical Design of Experiments”. *ACS Nano* 3, 1803-1812.

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NSF CMMI-0448774 and DMS-0706436



# Air Force Manufacturing Technology (ManTech)

## *Strategy and Trends*

*for*

## NSF Workshop on Nanomanufacturing

2-4 Nov 09

**Kermit Stearns**

Technical Director &  
Manufacturing Portfolio Manager  
Manufacturing Technology Division  
AFRL/RXM



*Integrity - Service - Excellence*



# Outline



- **Air Force ManTech Overview**
- **Planning/Strategy**
- **Technology Trends**



# AFRL Manufacturing Portfolio Overview



**Partnerships for Strong Industrial Base Capability for the Warfighter**

Warfighters



## Objectives

- **Reduced Costs** for Acquisition & Sustainment
- **Reduced Time** for Tech Transition / Manufacturing / Maintenance
- **Reduced Risk** when introducing **New or Improved System Capabilities**
- **Increased Availability** of technologies, materials, or components through shaping of industrial base

**Manufacturing & Industrial Readiness Core Competencies for the USAF**



+ Ind Base Assess • OSD Mfg S&T • DPA Title-III • DPAS



# Investment Framework AF ManTech & Ind Base Planning



## Acquisition Affordability & Producibility

- Solve Pervasive Mfg Issues
- Reduce Cost/Sched/Perf Risk

## Affordable S&T Transition

- Ensure Mfg Readiness of S&T
- Expedite Tech Transition

## Disruptive Mfg Technologies

- IB-wide Transformation
- High Impact in Critical Areas

## Industrial Base Assessments

- IB Situation Awareness
- ID Critical IB Issues/Opportunities

*Core Competencies: Mfg Readiness & IB Readiness*





# ManTech Investment Selection Criteria



## 1. Is it ManTech? *(a Go/No-Go Decision)*

- Enhances Manufacturability / Producibility of a Process or Component
- Beyond Reasonable / Normal Industry Risk
- Requirement Is Defense-essential or Defense-unique
- R&D Feasibility Established
- Current Technology Readiness Level (TRL) & MRL



**By:**

- Improving an Existing Manufacturing Process
- Establishing a New Manufacturing Process
- Exploiting Business Practices
- Expediting Transition of Emerging Technology

## 2. Warfighter Impact

- Significance to Warfighting Capability
- Magnitude of Impact: Capability, Cost, Cycle Time
- System Level Impact, Business Case

## 3. Stakeholder Support/Customer Motivation

- Commitment to Implementation Plan; Cost Share?

## 4. Pervasiveness: Multi-customer / Multi-system

- Strategic fit/balance with core ManTech philosophy



# Major On-going Programs AF ManTech & Industrial Base

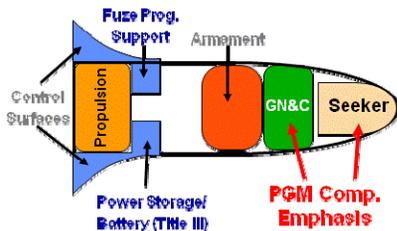


## AESA Radar



- Increased affordability for current/next gen AESA and conformal arrays

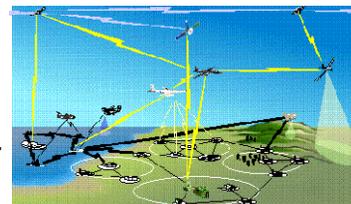
## Prec Guided Munitions



- Lowering costs and accelerating availability of advanced IMU & seeker technology to the warfighter

## Datalinks Components

- Increased affordability and production capacity of net centric warfare for ISR, weapons, and space



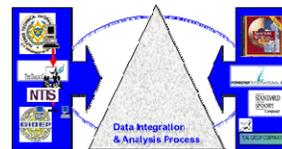
## Mfg Readiness Assessments

Material Solution Analysis				Technology Development		Engineering & Manufacturing Development			Production & Deployment
MRL 1 Item Mfg. Implications Identified	MRL 2 Mfg. Concepts Identified	MRL 3 Mfg. Proof of Concept Developed	MRL 4 Manufacturing Process in Lab. Environment	MRL 5 Component in Production Plant Environment	MRL 6 System or Subsystem in Production Representative Environment	MRL 7 System or Subsystem in Production Representative Environment	MRL 8 Production Ready for LAP	MRL 9 LMP Demonstrated Ready for PDP	MRL 10 PDP Demonstrated and Production Practices in place
PHL 1 Design Strategy Derived	PHL 2 Design Feasibility	PHL 3 Design of Concept	PHL 4 Hardware in Lab. Environment	PHL 5 Hardware in Plant Environment	PHL 6 Hardware in Plant Environment	PHL 7 Production Ready for LAP	PHL 8 System QA	PHL 9 System QA	PHL 10 System QA

Relationship to Technology Readiness Levels

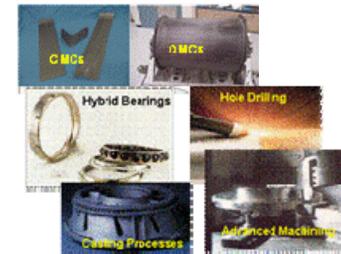
- Common language/standard for assessing manufacturing maturity – enables rapid, affordable production

## Industrial Base Assessments



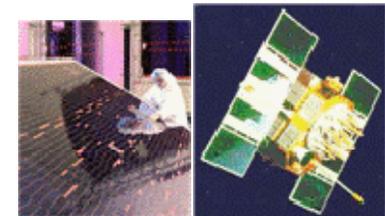
- Characterize IB for acquisition and technology decisions/investments

## Advanced Propulsion



- Fundamentally changing cost, weight, capability of turbine engines

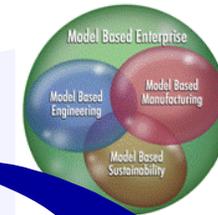
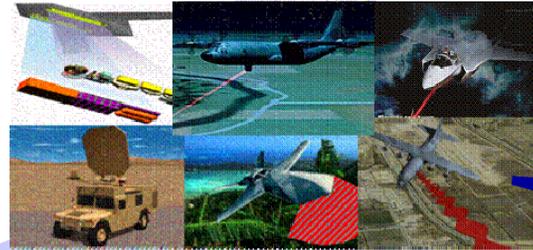
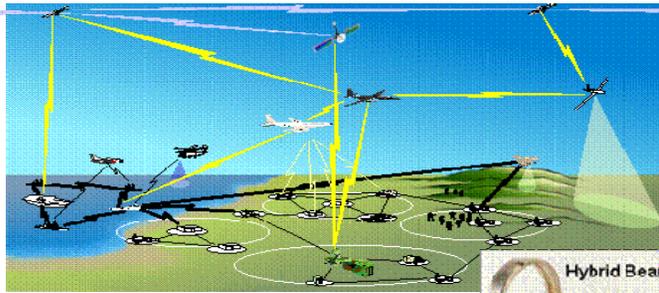
## Solar Cells



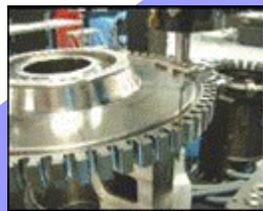
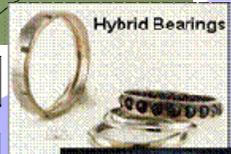
- Increased affordability and sustainability – new industrial base capability



# AFRL Manufacturing Portfolio Forecast



Pre-Concept Refinement			Material Solution Analysis	Technology Development			EMD			Production & Deployment
MRL 1	MRL 2	MRL 3	MRL 4	MRL 5	MRL 6	MRL 7	MRL 8	MRL 9	MRL 10	MRL 11
Define Mfg Requirements	Mfg Concept Development	Mfg Process Development	Material/Process Integration	Component Production	System Integration					
TEL 1	TEL 2	TEL 3	TEL 4	TEL 5	TEL 6	TEL 7	TEL 8	TEL 9	TEL 10	TEL 11
Define Mfg Requirements	Concept Development	Process Development	Material/Process Integration	Component Production	System Integration					



- Adv Mfg Propulsion Initiative
- Current/Next Gen AESA
- ISR & Wpns Datalinks Components
- Solar Cell Producibility
- Directed Energy Components
- High Velocity Depot Mx
- PGM Components
- Advanced Structures Initiative
- Engine Rotor Life Extension
- Mfg Readiness Assessments

**NEAR TERM (2009-2014)**

- Adv Mfg Propulsion Initiative
- Conformal AESA
- Transformational Comm
- Solar Cell Producibility
- Directed Energy Components
- High Velocity Depot Mx
- Advanced Structures Initiative
- Nano materials manufacturing ✓
- Model Based Enterprise
- Direct Digital Mfg
- Mfg Readiness Assessments

**MID TERM (2015-2020)**

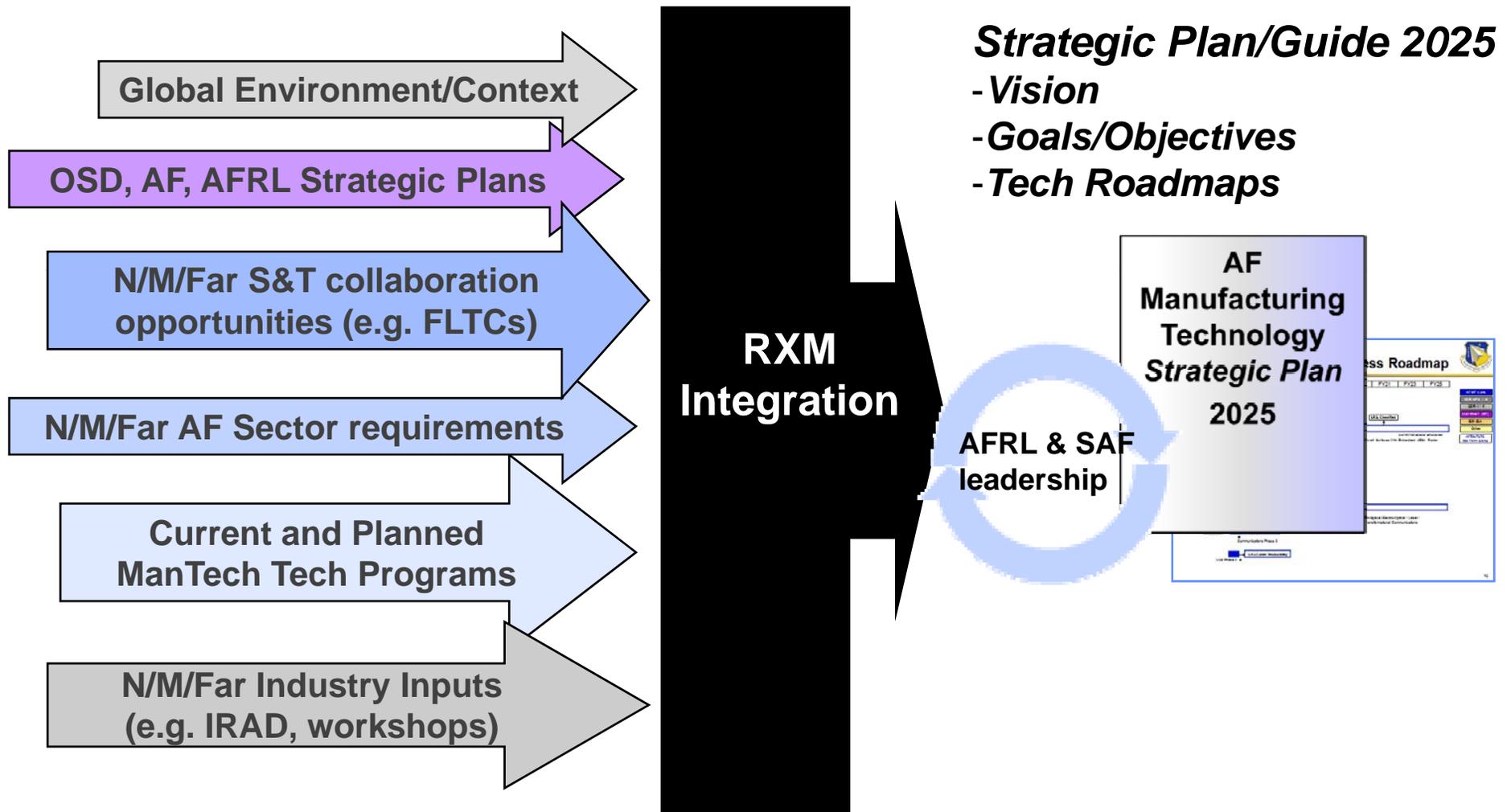
- Adv Mfg Propulsion Initiative
- Conformal AESA
- Transformational Comm
- Directed Energy Components
- High Velocity Depot Mx
- Advanced Structures Initiative
- Nano materials manufacturing ✓
- Model Based Enterprise
- Direct Digital Mfg
- Mask-less electronics mfg
- Tool-less design and mfg

**FAR TERM (2021+)**

**Sustained Investment for Lasting Impact on Industrial Base**



# Strategic Plan Formulation





# Potential Areas for Roadmaps



## Manufacturing Roles in AF Capability Trends

- C4ISR/Cyber (hardware)
- Stealth
- Advanced Comm
- Unmanned Air Systems
- Directed Energy

## Manufacturing Roles in AF Affordability and Efficiency Trends

- Energy/fuel
- Life Cycle Cost reductions
- Logistics footprint reductions
- Combat turnaround
- Depot turnaround

## Manufacturing Role in AFRL FLTCs

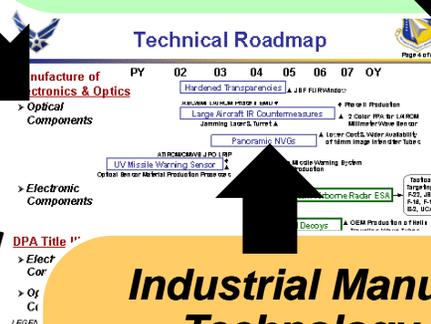
- Multi-Layer Sensing
- Precision Guided Submunitions
- Electric Laser
- Rapid Global Engagement
- Operationally Responsive Space

## Manufacturing Technology Solutions to IB Issues/Opps

- IR detectors
- Solar Cells
- Large scale composites and hybrids
- Stealth coatings
- Power tubes
- Solid state lasers

## Industrial Manufacturing Technology Trends

- Direct digital mfg
- Nano materials manufacturing
- Mask-less ICs
- Tool-less design and manufacturing
- Model-based Enterprise





# Sample of Industry Workshop Findings



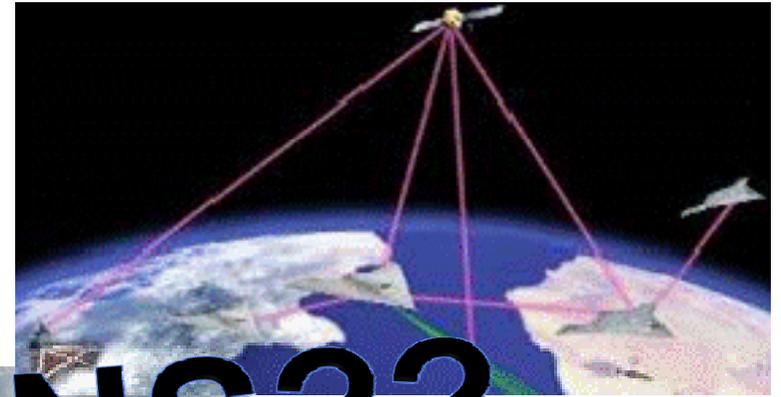
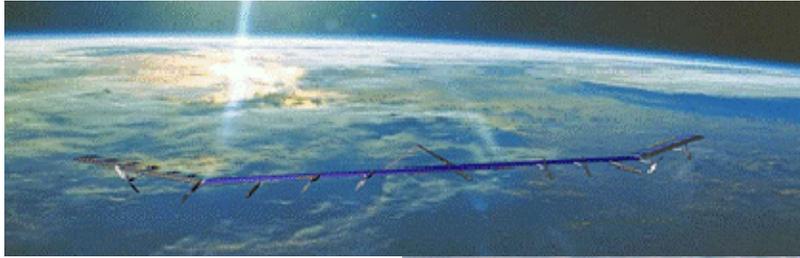
- **Overarching**
  - Vastly reduced cycle times and smaller lot sizes for future systems
  - Rapid response as an organizing principle
  - Energy lean manufacturing and green manufacturing
- **Information Integration**
  - Shop floor process (physics-based) modeling, in-situ awareness
  - Model-based design, manufacturing, support
  - Network-centric supply chain
- **Supply chains**
  - Proactive mgmt of industrial base issues
  - War-gaming and other supply chain simulation
- **Processing and Fabrication**
  - Direct digital mfg
  - Low cost durable tooling
  - Joining technologies
  - Self healing electronics and structures



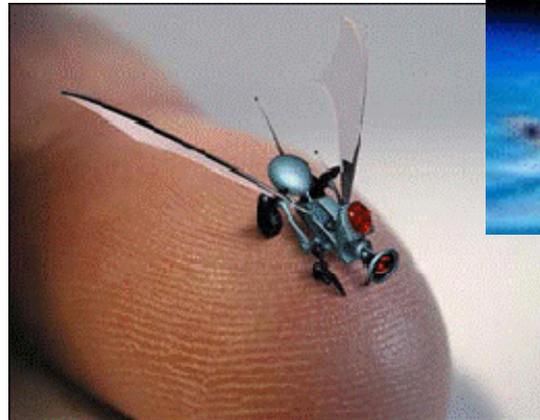
# *Draft Industry Workshop Products* **Desired Technical Capabilities**



- Tool-less electronics manufacturing
- **Lead Free Electronics Manufacturing Capability**
- Low Cost Manufacturing of Unitized, Multifunctional Structures
- **NDE Structural Technologies**
- Manufacturing processes for high bandwidth materials
- **Develop materials manufacturing techniques for thermal solutions**
- Shorter path to Certification for Propulsion Components
- **Push Advanced materials and process qualification into supply chain**
- Low-cost, affordable tools for low-rate manufacturing
- **Model Based Manufacturing Enterprise**
- Enabling Technologies for Network Centric Manufacturing
- **Direct Digital Manufacturing / “Instant Manufacturing “**
- Scale up of Hybrid / Alternative Power Generation
- ✓ **Control of Manufacturing at Small Scale (Nano)**
- Sustainable Manufacturing Processes and Infrastructure
- **Early design tradeoffs for manufacturability**



**QUESTIONS??**



# NSF Workshop on Sensing and Prognostics for Scalability of Nanomanufacturing

## *Group 2: Quality and Reliability*

David W. Coit

Department of Industrial & Systems Engineering

Rutgers University

Piscataway, NJ, USA

November 3, 2009

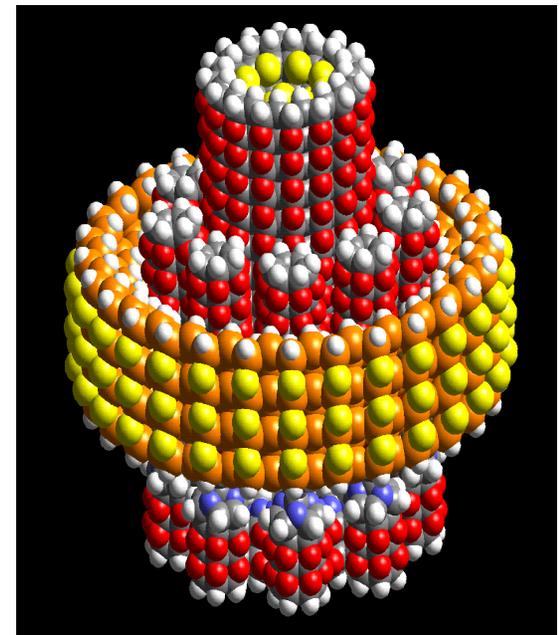


RUTGERS

# Nano-technology Quality and Reliability

“High reliability and high yield are necessary to guarantee the advancement and utilization of micro & nano products. Reliability researchers need to be *energized* to tackle the very real problems that we face in the nano-rich world.”

Way Kuo, 2006



# Quality and Reliability: Questions to Group

1. What are the quality and reliability issues in nanomanufacturing? How do they differ from those in conventional manufacturing?
2. What is the state-of-the-art in quality and reliability in nanomanufacturing?
3. What are the imperatives for quality and reliability?
4. What are the targets for quality and reliability?
5. What are the barriers to achieving targets for quality and reliability?
6. What are the recommendations for achieving targets for quality and reliability?

# State-of-the Art: Nano-technology Reliability

1. S. Bae, S.-J. Kim, W. Kuo & P. Kvam (2007), "Statistical models for hot electron degradation in nano-scaled MOSFET devices," *IEEE Trans. Reliability*
2. P. Lall, S. Islam, J. Suhling & G. Tian (2005), "Nano-Underfills for High-Reliability Applications in Extreme Environments," *Electronic Components and Technology, ECTC '05 Proceedings*
3. R. Ritchie, C. Muhlstein & R. Nalla (2004), "Failure by fracture and fatigue in nano and bio materials," *International Journal Series A—Solid Mechanics and Material Engineering*
4. G. Sivalingam & G. Madras, "Photocatalytic degradation of poly (bisphenol-A-carbonate) in solution over combustion-synthesized TiO<sub>2</sub>: Mechanism and kinetics," *Applied Catalysis A—General*
5. W. Lin, T. Wu, Y. Tsai, L. Du & Y. King (2005), "Reliability evaluation of class-E and class-A power amplifiers with nanoscaled CMOS technology," *IEEE Trans. Electron Devices*
6. Y. Liu, A. Sadat, and J. S. Yuan (2005), "Gate oxide breakdown on nMOSFET cutoff frequency and breakdown resistance," *IEEE Trans. Device and Materials Reliability*
7. etc.

# State-of-the Art: Nano-technology Reliability

## Summary of Research Approaches

- Degradation modeling (many researchers)
- Nano-system redundancy allocation/optimization (e.g., Bhaduri & Shukla, 2004, 2005)
- Fault tolerant design (e.g., Schmid & Leblecici, 2009)

## Critical Issues

- Understanding physical behavior relating to failure mechanisms at the nano-level
- Impact of manufacturing variability on product reliability
- Interactions among nano-structures
- Dependent nano-component behavior
- Heterogeneous nano-structures

# State-of-the Art: Nano-technology Reliability

## Analytical and Modeling Needs

- Need for physical models and combined statistical/physical models
- Integrated models combining manufacturing variability and product life (*improvement*)
- Propagation of uncertainty within nano-design components (*robustness*)
- Effective fault tolerance and redundancy design approaches (*compensation*)
- Accelerated life testing methods and models
- Adaptable but consistent reliability methodologies to support larger scale development

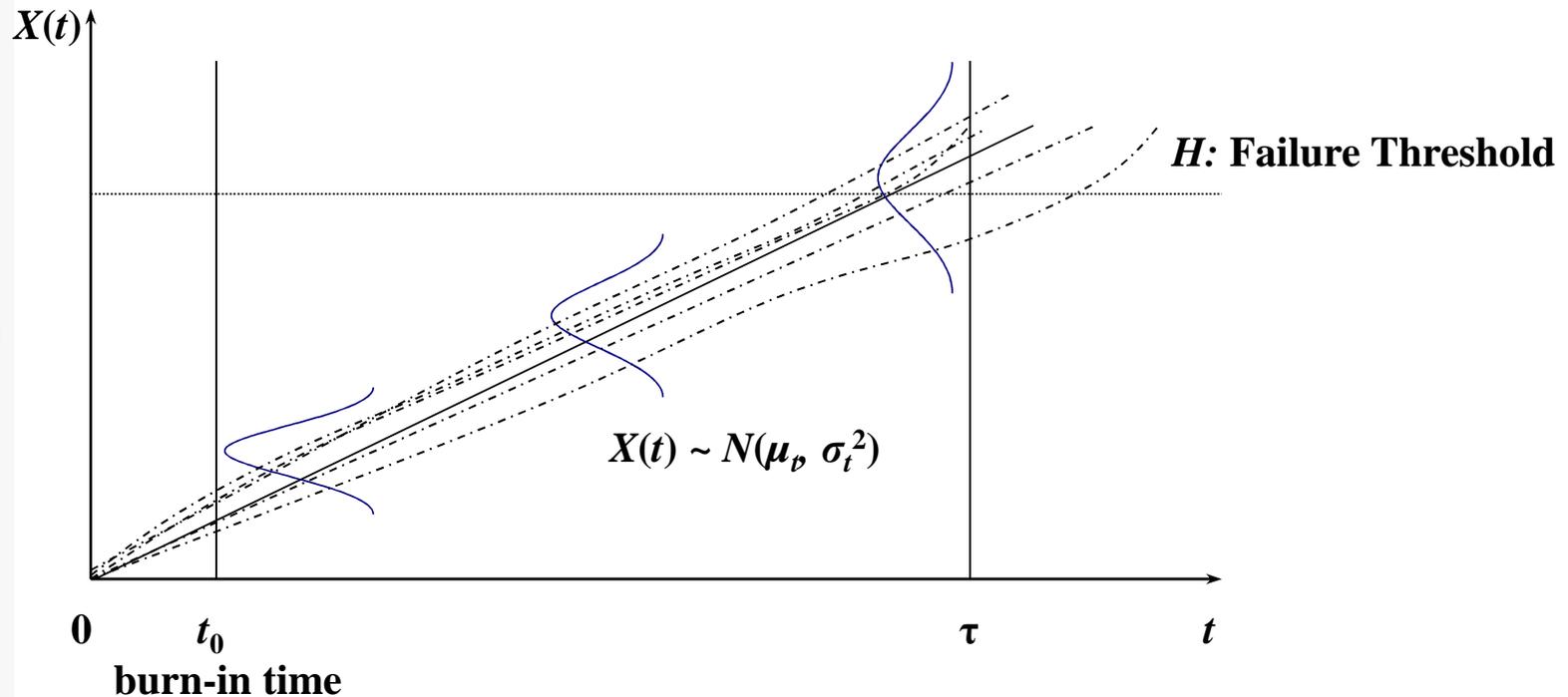
# Nano-technology Reliability

Generation	Nano-Products	Reliability models/analyses needed
1 <sup>st</sup> Generation	Passive nanostructures	Failure modes/mechanisms Degradation models Accelerated testing
2 <sup>nd</sup> Generation	Active nanostructures	Integration of process variability & product life
3 <sup>rd</sup> Generation	Systems of nanosystems	Redundancy optimization Models for variability propagation Fault tolerance design concepts
4 <sup>th</sup> Generation	Molecular nanosystems	<i>All the above &amp; more</i>

# NEMS/MEMS Reliability Models Based on Degradation Trends

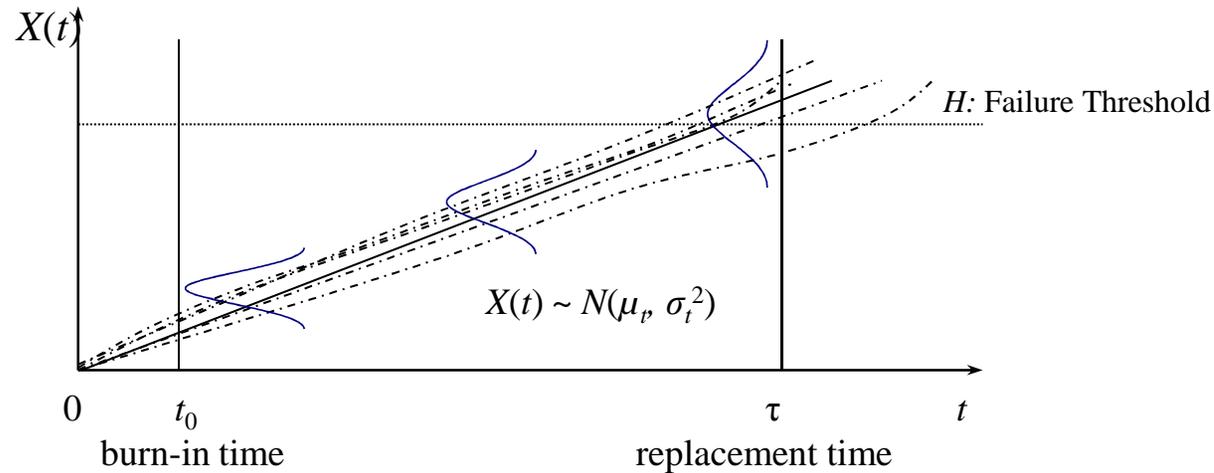
## Nano-technology degradation models

- MOSFET nano-degradation (Bae et al., 2007)
- Photodegradation (Sivalingham & Madras, 2004)
- Leakage current through oxide (Chester et al., 2004)



# Degradation-based Failure Time Distribution

(Peng, Feng & Coit, 2009)



MEMS Example (Peng, Feng & Coit, 2009)

- Reliability Function

$$R(t) = P\{X(t) < H\} = \int_0^H f_{X(t)}(x; t) dx = \Phi\left(\frac{H - \mu_t}{\sigma_t}\right)$$

- Density Function: Two-Parameter Bernstein Dist.

$$f_T(t) = -\frac{dR(t)}{dt} = \frac{H}{\sqrt{2\pi b t^2}} e^{-\frac{(H-at)^2}{2b^2 t^2}}$$

$$a = 2\pi c \mu_r \mu_F \text{ and } b = \sqrt{(2\pi c)^2 (\sigma_r^2 \sigma_F^2 + \sigma_r^2 \mu_F^2 + \mu_r^2 \sigma_F^2)}.$$

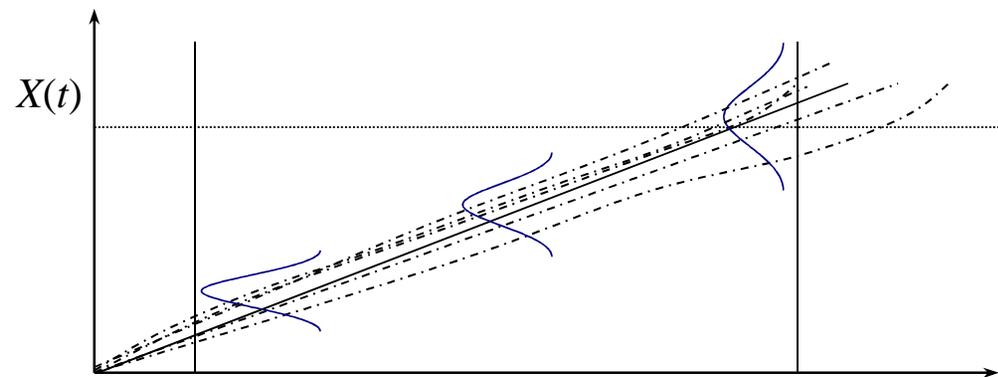
# Conventional Methods for Quality & Reliability Are Often Not Appropriate

## Conventional Methods

- De-coupled quality & reliability analyses – **quality and reliability are often considered sequentially and/or independently**
- Homogeneous populations with *iid* failure times

## Problems with Conventional Methods

- There is an inherent link between manufacturing variability and product reliability
- Nano-devices failure times may not be *iid*
- Reliability analysis and improvement must be addressed considering the link between manufacturing variability and failure time

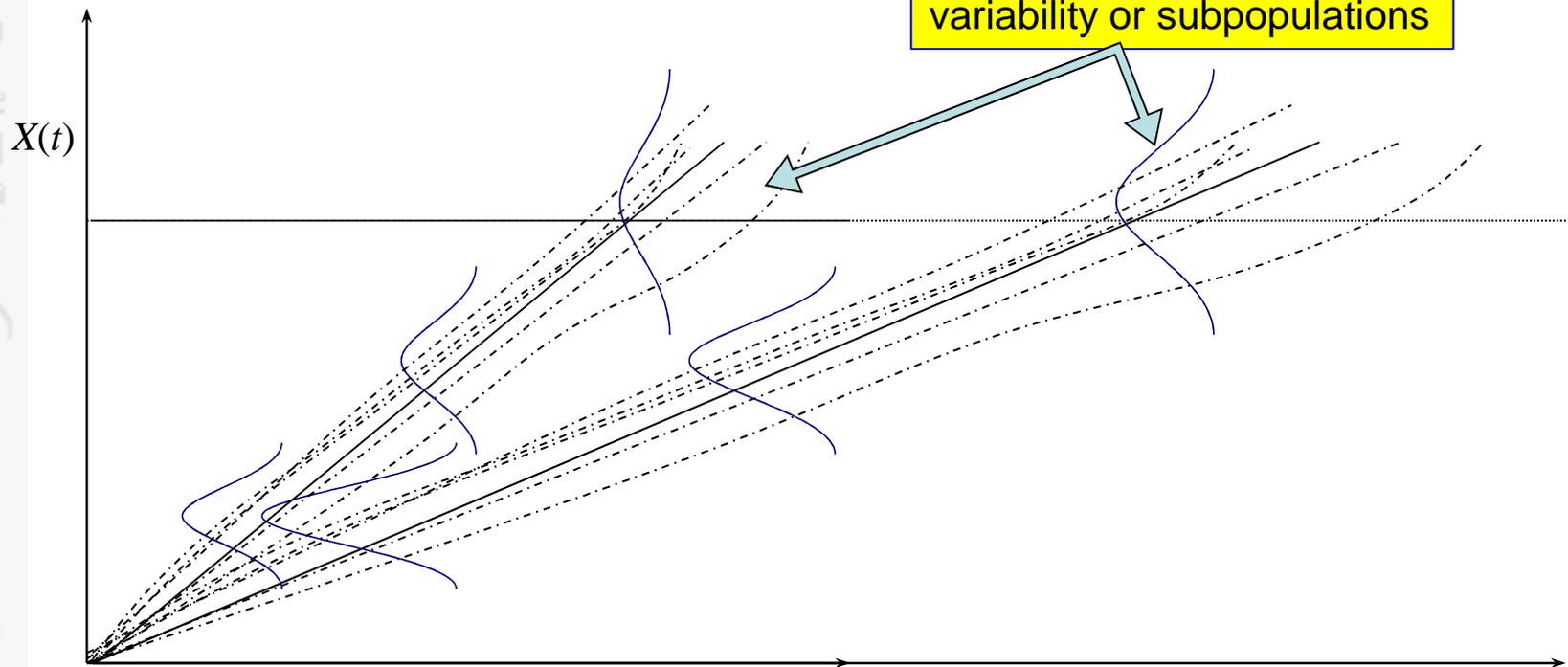


# Conventional Methods for Quality & Reliability Are Often Not Appropriate

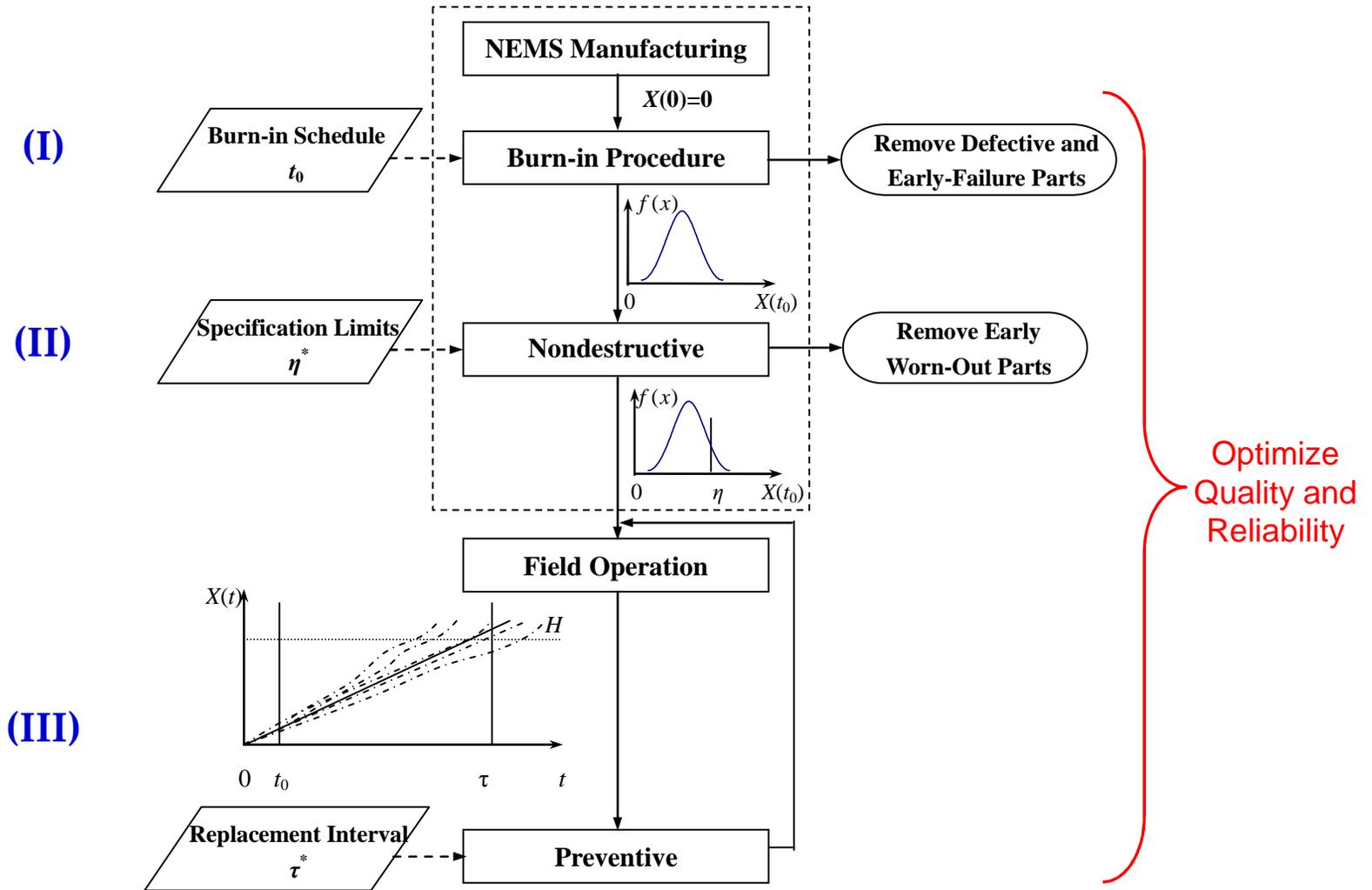
Reliability models & failure rates based on projected degradation trends

- Representative of the *marginal* distribution of failure time,  $f_T(t)$
- Neglects specific differences within sub-populations or individual units

Joint or conditional failure time distributions may be more applicable for reliability improvement,  $f_T(t|\mathbf{x})$ ,  $\mathbf{x}$  = vector for variability/ process variables



# Integrated Methodology for NEMS/MEMS Quality & Reliability



Peng, H., Feng, Q., Coit, D. (2009), "Simultaneous Quality & Reliability Optimization for Microengines Subject to Degradation," *IEEE Transaction on Reliability*.

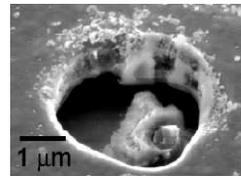
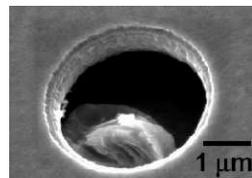
# Degradation Model Example

(Peng, Feng & Coit, 2009)

- $X(t; \beta)$ : degradation at time  $t$ 
  - Specification of the function
  - Specification of fixed and random parameters in  $\beta$
- Functional form can be obtained based on *physical models* or *empirical observations*
- The wear volume has a linear degradation path

$$X(t; r, c, F) = 2\pi rcFt$$

- $c$  is the coefficient related to wear and hardness of the material (fixed)
- $r$  is the radius of the pin joint (random)
- $F$  is the force between the contacting surfaces (random)

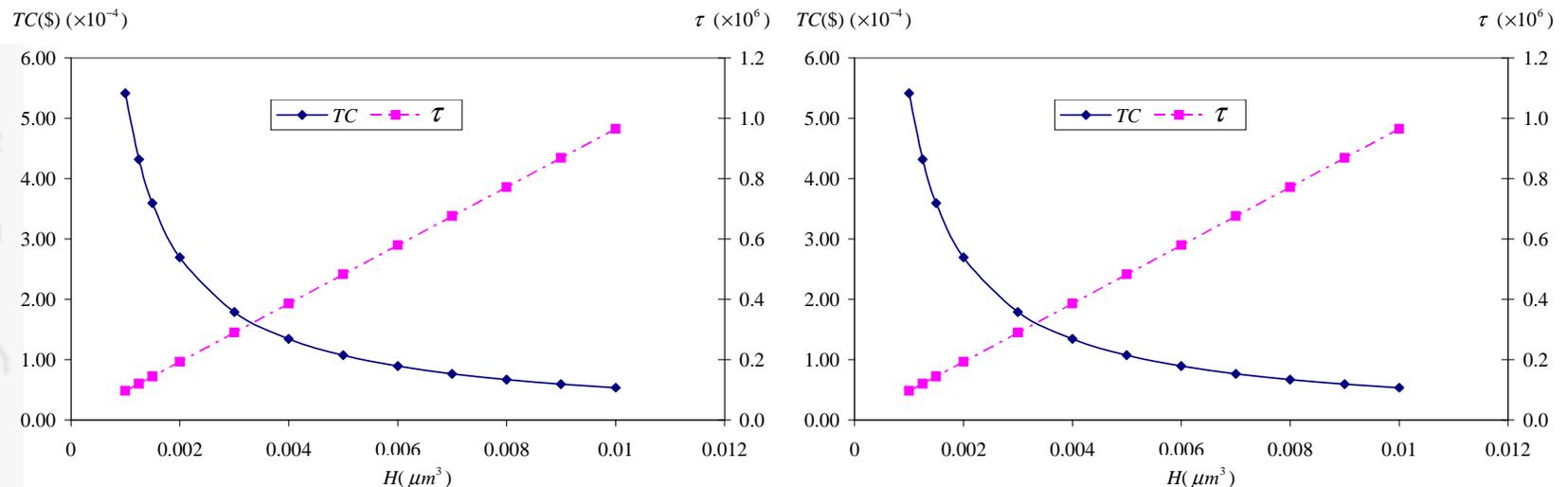


gear and pin joint

# Degradation Model Example

(Peng, Feng & Coit, 2009)

- Optimization model solved to minimize cost considering a quality-loss approach considering manufacturing variability and reliability simultaneously



# State-of-the Art: Nano-manufacturing Quality

1. K. Kim, S. Kim & H. Kim (2005), "Applying the Taguchi method to the optimization for the synthesis of TiO<sub>2</sub> nanoparticles by hydrolysis of TEOT in micelles," *Colloids and Surfaces A: Physicochem. Eng. Aspects*
2. Nazzal, Nutan, Palamakula, Shah, Zaghoul & Khan (2002), "Optimization of a self-nanoemulsified tablet dosage form of Ubiquinone using response surface methodology: effect of formulation ingredients," *International Journal of Pharmaceutics*
3. R. Ganesan, T. Das, A. Sikder & A. Kumar (2003), "Wavelet-Based Identification of Delamination Defect in CMP (Cu-Low *k*) Using Nonstationary Acoustic Emission Signal," *IEEE Trans. on Semiconductor Manufacturing*
4. R. Ganesan, T. K. Das, A. K. Sikder & A. Kumar (2003), "Wavelet-based identification of delamination defect in CMP (Cu-Low *k*) using nonstationary acoustic emission signal," *IEEE Trans. Semiconductor Manufacturing*
5. A. H. Barber, I. Kaplan-Ashiri, S. R. Cohen, R. Tenne, and H. D. Wagner, "Stochastic strength of nanotubes: An appraisal of available data," *Composites Science and Technology*
6. etc.

# State-of-the Art: Nano-manufacturing Quality

## Summary of Research Approaches

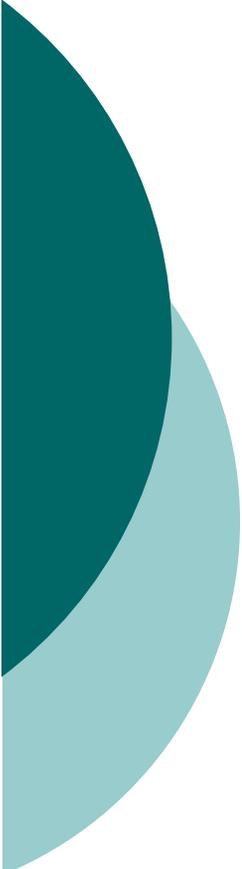
- Design of Experiments (DOE)
- Response Surface Methods
- Feedback based on in-process data

## Critical Issues and Needs

- Significant manufacturing variability
- Standardized parameters and associated testing procedures needed
- Propagation of variability between stages of manufacturing
- Adaptable but consistent quality tools to support larger scale development

# Quality and Reliability: Questions to Group

1. What are the quality and reliability issues in nanomanufacturing? How do they differ from those in conventional manufacturing?
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# Sensing and Prognostics for Nanomanufacturing

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Storrs, CT 06269

Email: [RGao@engr.uconn.edu](mailto:RGao@engr.uconn.edu)

**NSF Workshop on Sensing and Prognostics for Scalability of Nanomanufacturing**

November 2-4, 2009, Boston, MA

# Introduction

## ■ Sensing for Nanomanufacturing

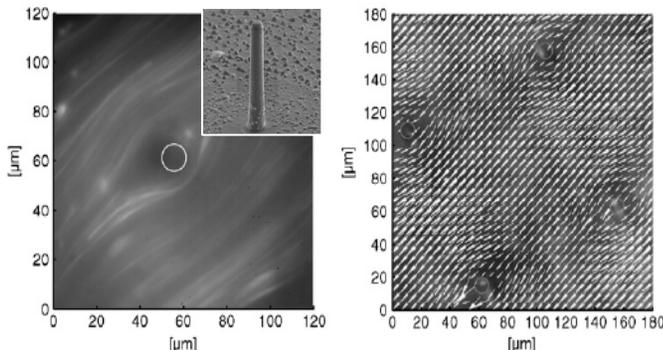
### ✓ Nano-Newton Force Measurement

- *Prototype cantilevers for SI traceable nanonewton force calibration*, Gates et al., Meas. Sci. & Technol., 2006.
- *Nanonewton drag sensor based on flexible micro pillars*, Groβ e et al., Meas. Sci. & Technol., 2006.

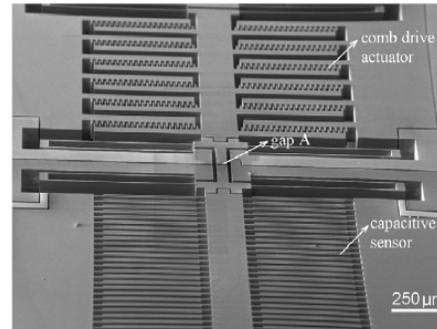
### ✓ Displacement / Deformation Monitoring

- *Silicon cantilever sensor for micro-nano scale dimension and force metrology*, Peiner et al., Microsys. Technol., 2008.
- *A high sensitivity and quasilinear capacitive sensor for nano mechanical testing applications*, Zhang et al., J. Micromech. Microeng., 2009.

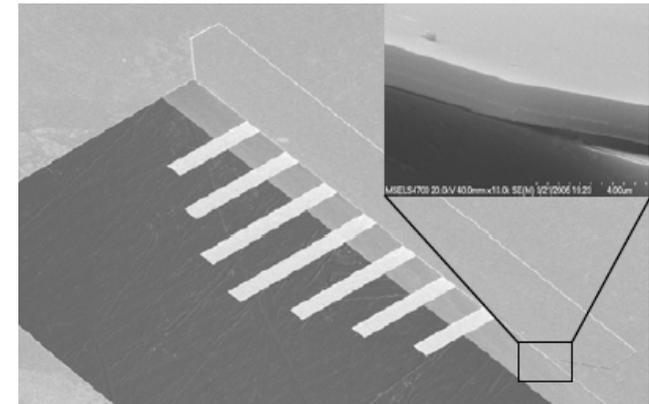
### ✓ Flow Rate, Surface Roughness, ....



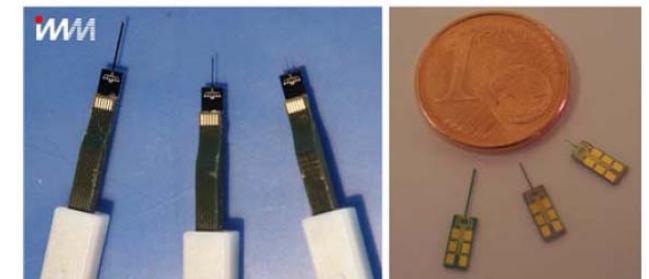
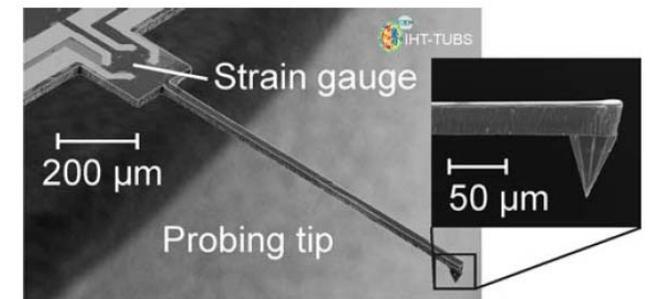
Micropillar for drag measurement (Groβ e, 2006)



On chip sensor (Zhang, 2009)



Cantilever array device (Gates, 2006)



Prototype displacement sensors (Peiner, 2008)



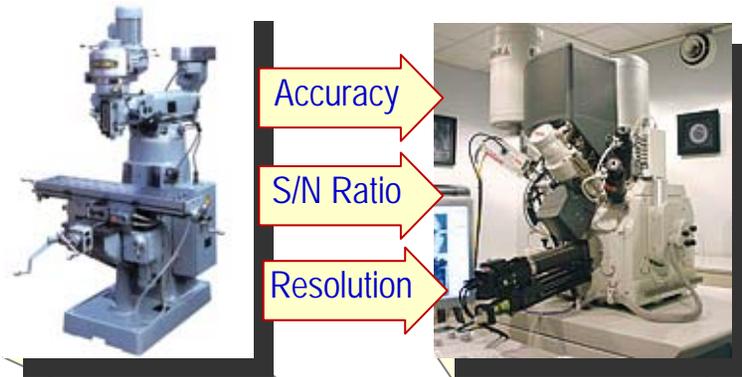
EMSL

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*Sensing & prognostics: macro ⇒ micro ⇒ nano scale*

# Scalability Challenges

## Nanomanufacturing Process



	Conventional Machining	Nano-Machining
Machining Unit	Multi-crystals	Atomic cluster
Feature Size	1 mm ~ 10 $\mu$ m	0.1 $\mu$ m ~ 1 nm
Part weights	1 g	0.1 mg

## Sensing Methods

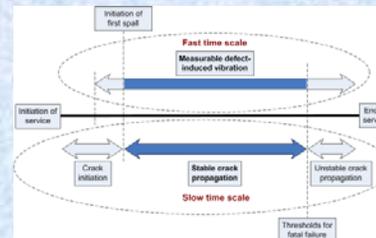
- ✓ Self-Powering
  - RF/Acoustic
- ✓ Wireless
- ✓ Energy Efficiency
  - Data compression
  - Adaptive sampling
  - Comm. protocol

## Signal Processing

- ### Time-Frequency
- Wavelets
  - Empirical Mode Decomposition
- ### Spatio-Temporal
- Numeric surface interpolation
  - Force/Pressure distributions

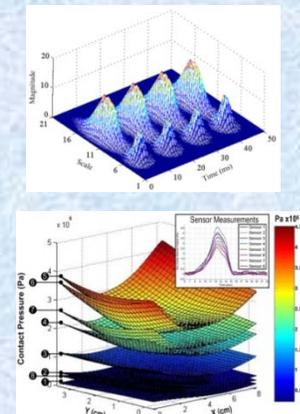
## Prognosis

- ✓ Multi time scale modeling



- ✓ Principal feature analysis
- ✓ Spatial descriptors

## Feature Extraction



Quality Control & Process Improvement

Defect Detection & Process Control

## Challenges in Nano-Scale Sensing

- High Sensitivity & Noise Immunity;
- Uncertainty in Measurement;
- Compact Size & High Flexibility.

## Research Issues:

- Multi-scale System Modeling;
- Nonstationary Signal Processing;
- Sensor Interface with Host Structure;
- Energy Efficient Data Transmission.

Observability & Knowledge Base



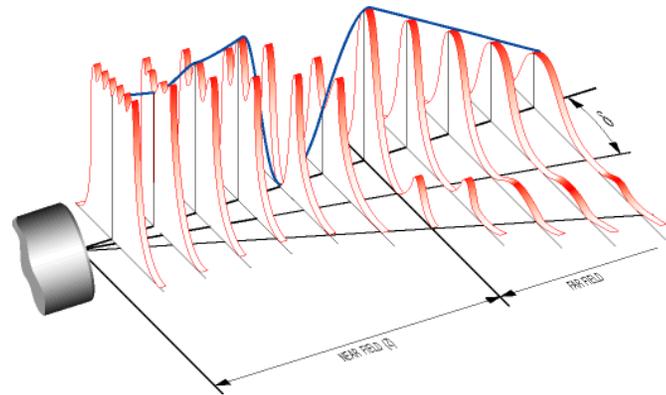
**EMSL**

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# Sensing and Communication

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- ✓ Energy Harvesting
- ✓ Data Transmission Methods
- ✓ Energy Efficiency



# Energy Harvesting

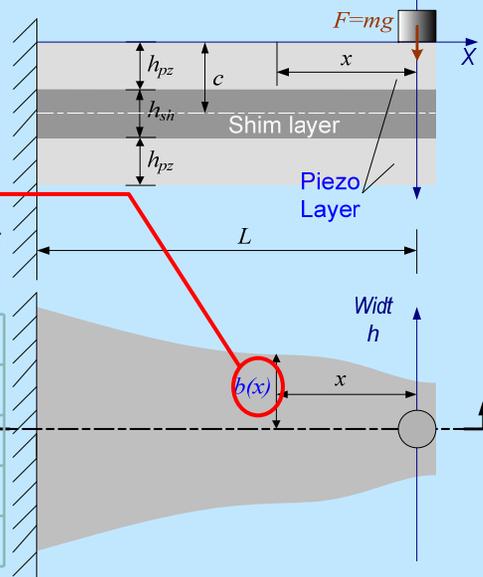
## Structure Optimization

Energy

$$E_{en}(b) = \int \frac{\sigma^2 d_{31}^2 h_{pz}}{2\epsilon} dA$$

$$= \frac{F^2 d_{31}^2 c h_{pz}}{4\epsilon\alpha} \int_0^L \frac{x^2}{b(x)} dx$$

A	Area of beam
$h_{pz}$	Thickness of piezoelectric layer
$h_{sh}$	Thickness of shim layer
$\sigma$	Mechanical stress
$\epsilon$	Permittivity constant



- Boundary Condition:  $J_1(b) = 2 \int_0^L b(x) dx = A$
- Lagrange Function:  $F(b) = \frac{x^2}{b(x)} + \lambda b(x)$

Given *fixed* volume, determine  $b(x)$  to maximize energy output.

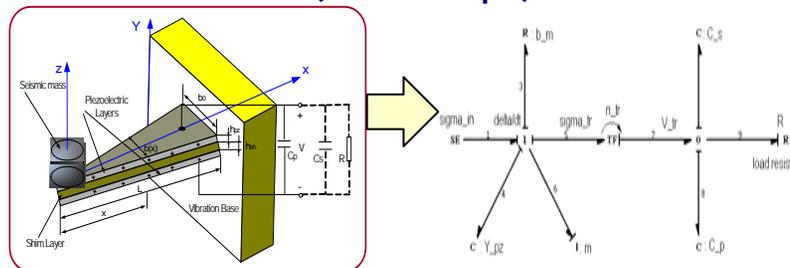


➤ Maxima exists when beam is triangular

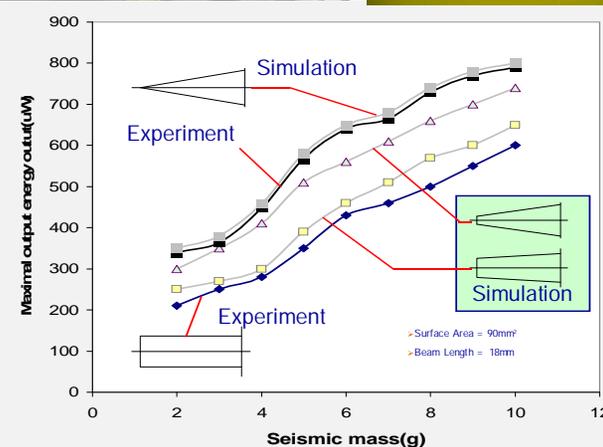
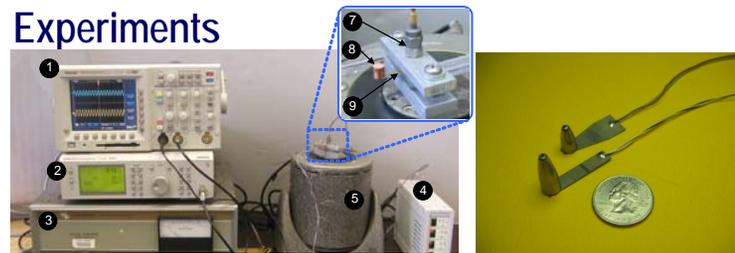
$$E_{max} = \frac{F^2 c^2 d_{31}^2 h_{pz} L^4}{8A\epsilon\alpha^2}$$

52% increase in output comp. with rectangular beam

## Simulation Model (Bond Graph)



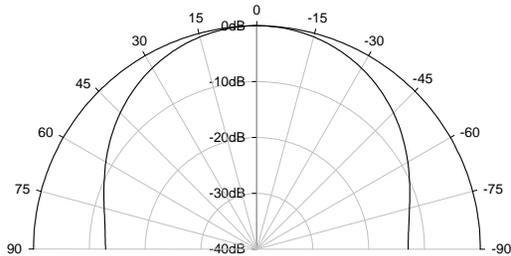
## Experiments



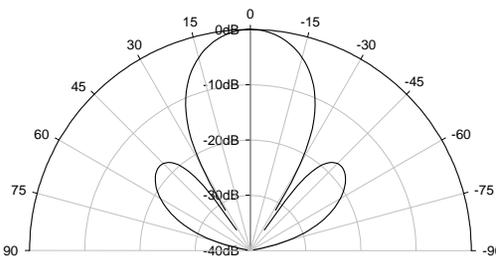
# Acoustic-Based Wireless Transmission

Transmitting Data from within RF-Shielded Environment:

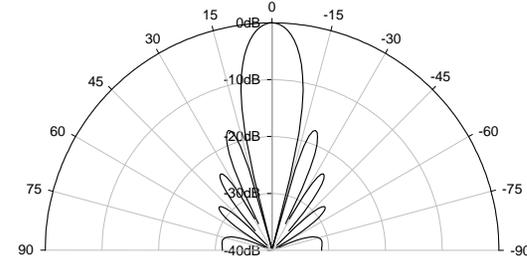
Angular dependence of ultrasonic field: 
$$P(r, \theta) = \sqrt{2} \left| \frac{\rho c}{2} U_0 \frac{a}{r} ka \left[ \frac{2J_1(ka \sin \theta)}{ka \sin \theta} \right] \right|$$



➤  $ka = 3, DI = 9.16 \text{ dB}$



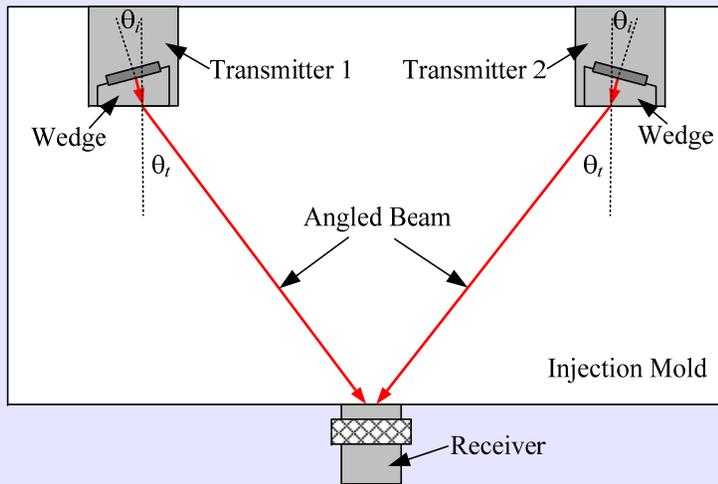
➤  $ka = 7, DI = 16.99 \text{ dB}$



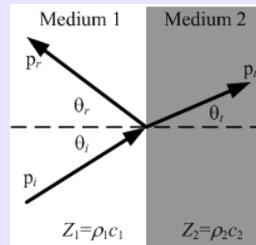
➤  $ka = 15, DI = 23.49 \text{ dB}$

$$k = \frac{\omega}{c} = \frac{\text{radian frequency}}{\text{sound velocity}}$$

*Increase of frequency improves the directionality of the acoustic wave*

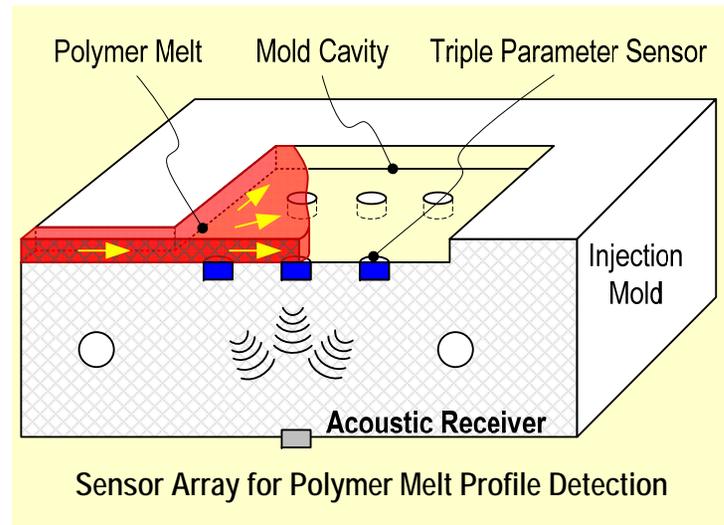


Reflection and refraction at interface



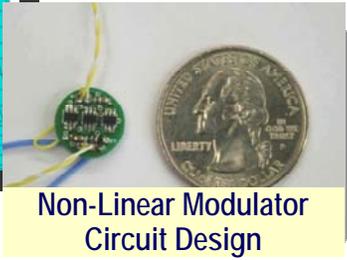
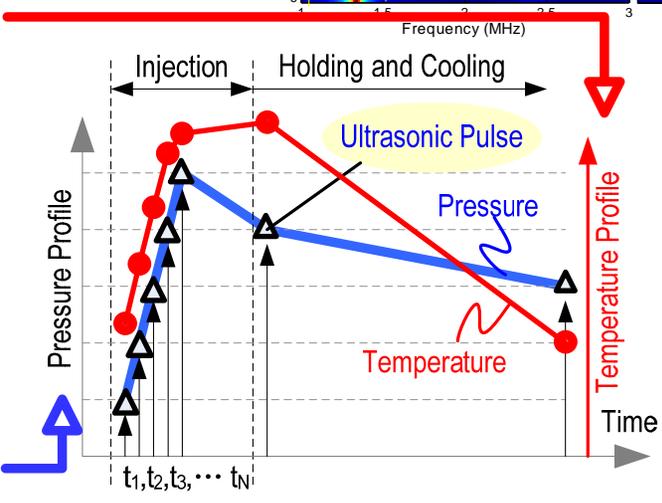
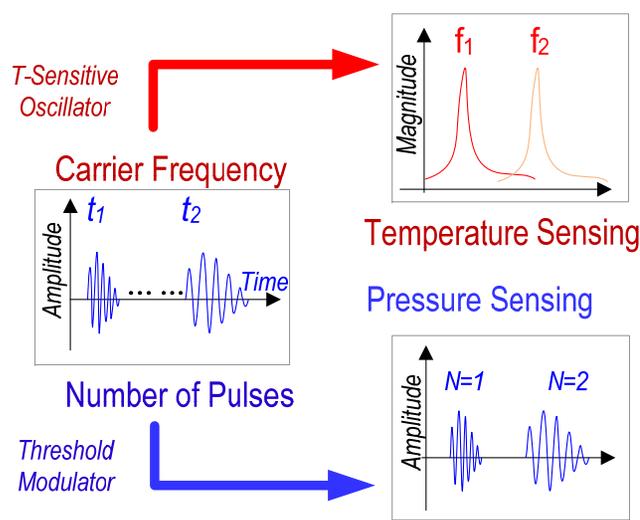
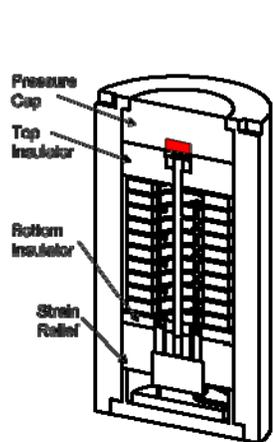
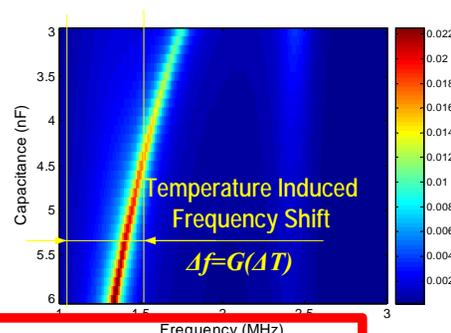
Determine angle of incidence and refraction

$$\frac{\sin(\theta_r)}{\sin(\theta_t)} = \frac{c_1}{c_2}$$



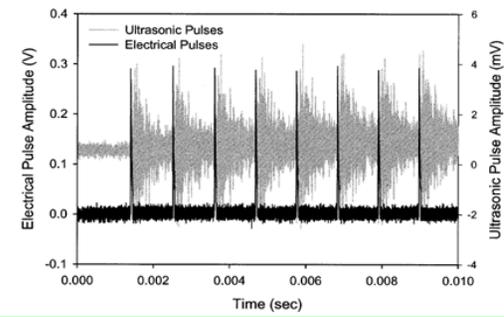
# Acoustic Signal Modulation

- Self-energized *dual sensing* method
  - ❖ Temperature measured by shift of ultrasound carrier frequency;
  - ❖ Pressure converted to ultrasonic *pulse* trains.



➤ **Dual-Parameter** measurement from a single sensor package;

➤ Improves process **observability** with minimum embedding cost.

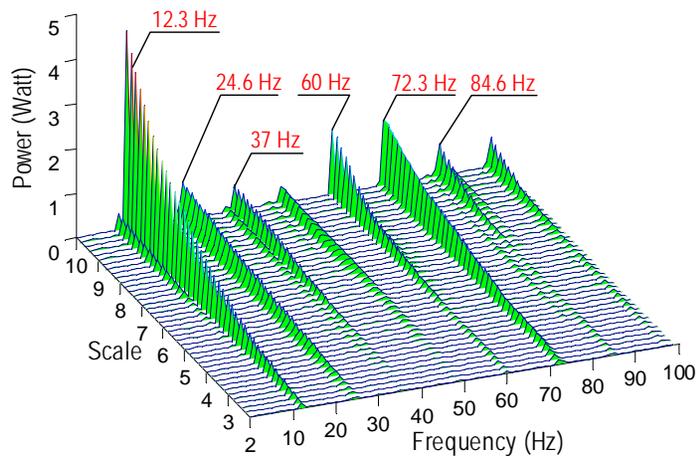
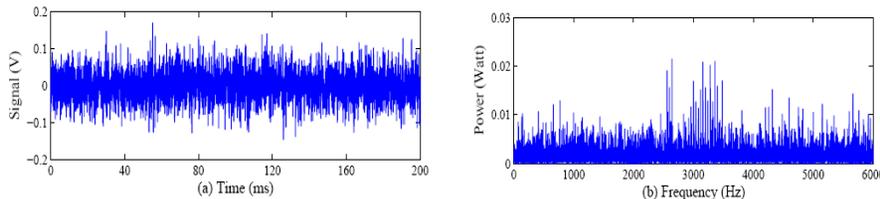


# RF-Based Wireless Transmission

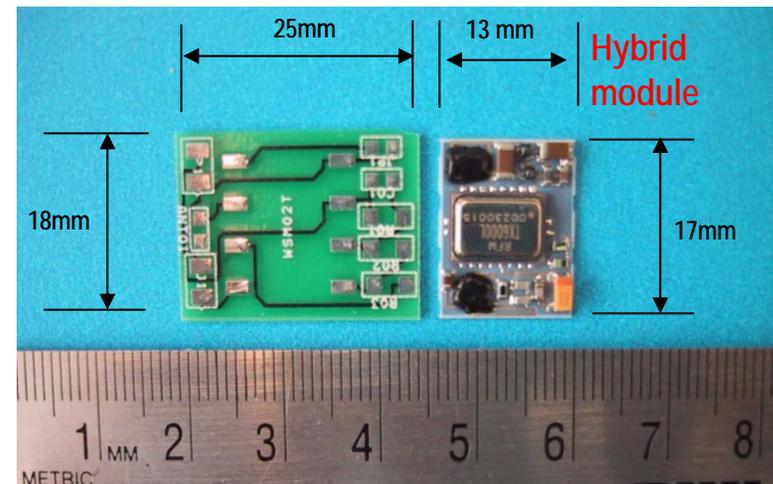
- Modulation Scheme:
  - CDMA, PSK, PCM
- Issues:
  - Amplification of low S/N signals associated with micron-level feature size;
  - Sensor miniaturization.

## Modulation Schemes: S/N & Bandwidth

	S/N ratio	Bandwidth
AM	$SNR_{AM} = n \frac{P_T}{N_0 W}$	$BW_{AM} = 2 f_m$
FM	$SNR_{FM} = 3\beta^2 \frac{P_m}{\max m^2(t)} \times \frac{P_T}{N_0 W}$	$BW_{FM} = 2 f_m (\beta + 1)$
PCM	$p_e = \frac{1}{2} \operatorname{erfc}(\sqrt{n \times SNR_c})$	$BW_{PCM} = 2 f_s N$



## Hybrid-Transceiver Design



R. Gao and P. Huenerberg, "Design of a CDMA-based wireless data transmitter for embedded sensing", *IEEE Transactions on Instrumentation and Measurement*, Vol. 51, No. 6, pp. 1259-1265, December, 2002.

# Energy-Efficient Protocol

- Additive Increase Multiplication Decrease (AIMD)

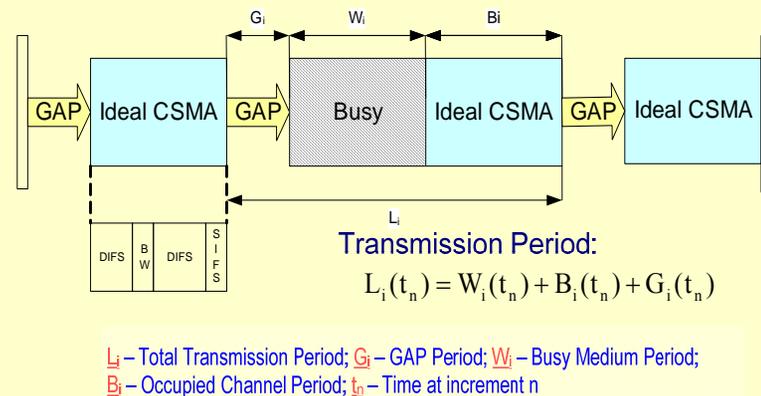
## AIMD Protocol

- Dynamic Gapping Window (GAP) between ideal CSMA
- Fixed Back-off Window

Channel Occupancy Ratio

$$R_i(t_n) = \frac{B_i(t_n)}{L_i(t_n)}$$

$$R_i(t_{n+1}) = \begin{cases} \text{if Success: } R_i(t_n) + \alpha_i(t_{n+1} - t_n) \\ \text{if Failure: } (R_i(t_n) + \alpha_i(t_{n+1} - t_n)) \cdot (1 - \beta_i) \end{cases}$$

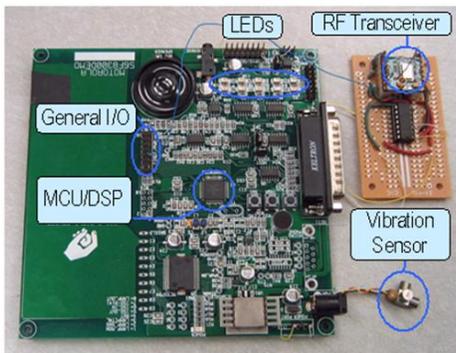


Collision Rate and Energy Consumption:

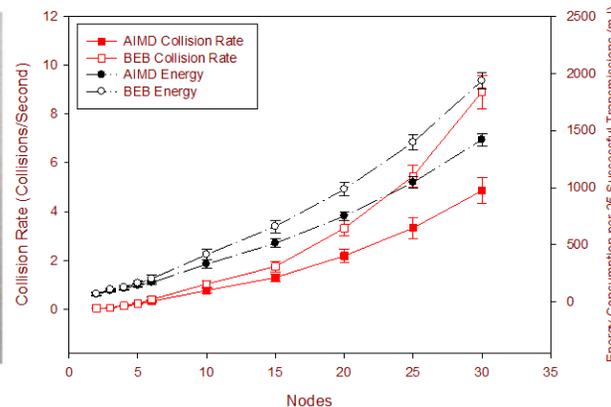
$$\lambda_{ij} = \zeta \cdot \frac{E[COR_i]}{CA_i} \cdot \frac{E[COR_j]}{CA_j}$$

$$\lambda_i = \zeta \cdot \frac{E[COR_i]}{CA_i} \cdot \sum_{j \neq i} \frac{E[COR_j]}{CA_j}$$

- $\lambda_i$  – Collision rate of node i;
- $\lambda_{ij}$  – Collision rate of nodes i and j;
- $COR_i$  – Channel Occupancy ratio;
- $CA_i$  – Aggregate channel time of node i;
- $\zeta_i$  – Correlation coefficient.



Collision Rate and Energy Consumption vs Node Population



- Increased energy savings achieved by AIMD protocol as number of nodes increases;
- Collision rate is mitigated using the AIMD protocol, allowing more efficient communication among sensor nodes.

# Energy-Efficient Data Coding

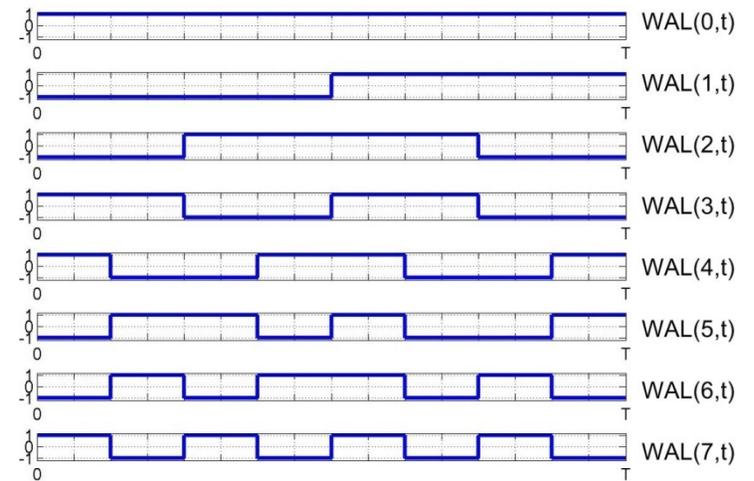
- Walsh Transform

Compress data for reduced communication energy

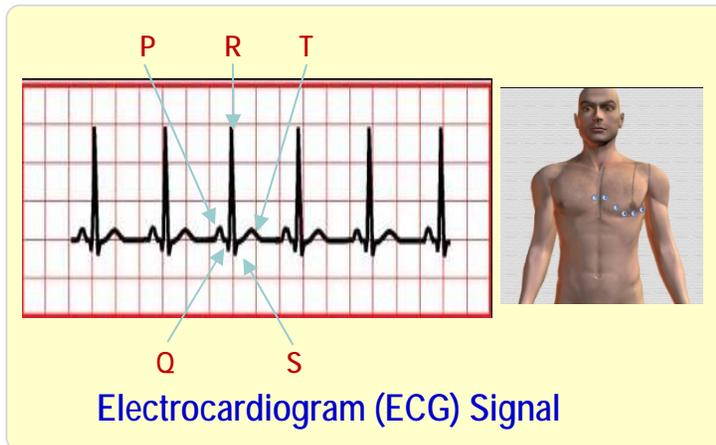
$$WAL(N, T) = WAL(n_{p-1}, n_{p-2}, \dots, n_0; t_{p-1}, t_{p-2}, \dots, t_0)$$

$$= \prod_{r=0}^{p-1} (-1)^{n_{p-1-r} (t_r + t_{r+1})}$$

$WAL$  – Walsh Function       $n_{p-1}, n_{p-2}, \dots, n_0$  –  $N$  expressed in binary notation  
 $N$  – Function number       $t_{p-1}, t_{p-2}, \dots, t_0$  –  $t$  expressed in binary notation  
 $t$  – Normalized time       $i, j$  – Indices  
 $N = 2^p$



First 8 Walsh Functions in increasing order of zero-crossings

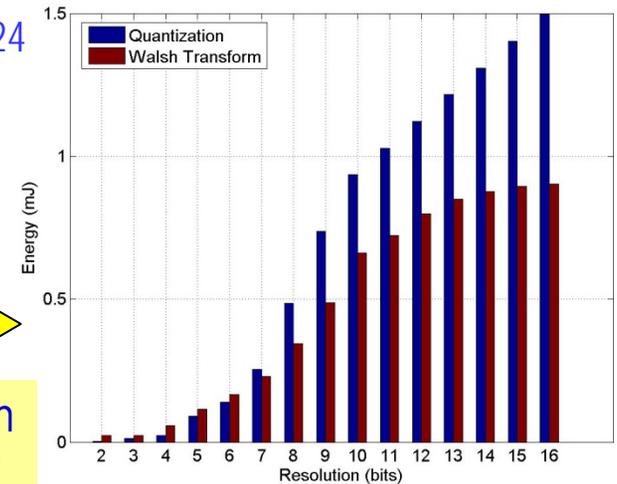


To transmit an ECG signal, 1024 samples;

- Raw signal: 0.917 mJ;
- Quantization: 0.487 mJ;
- Walsh coding: 0.274 mJ.



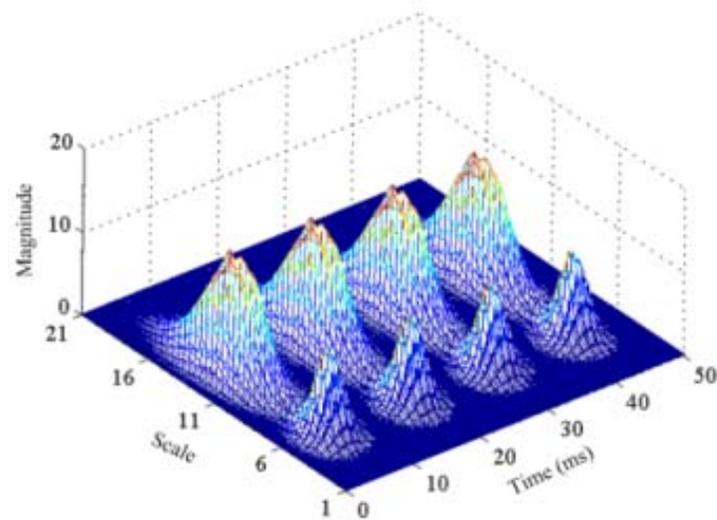
Good data resolution with less transmission energy



# Diagnosics & Prognostics

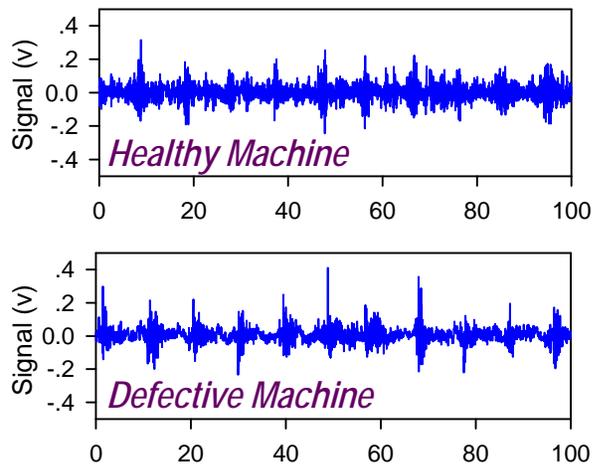
---

- ✓ Non-Stationarity and Non-Linearity
- ✓ Pressure Surfaces
- ✓ Multi-Time Scale



# Feature Extraction

- Features (e.g. energy value) extracted from vibration data used as indicators for defect estimation at the incipient stage.



Not Differentiable in Freq. Domain due to Low SNR



Frequency-Scale Domain

Wavelet Transform

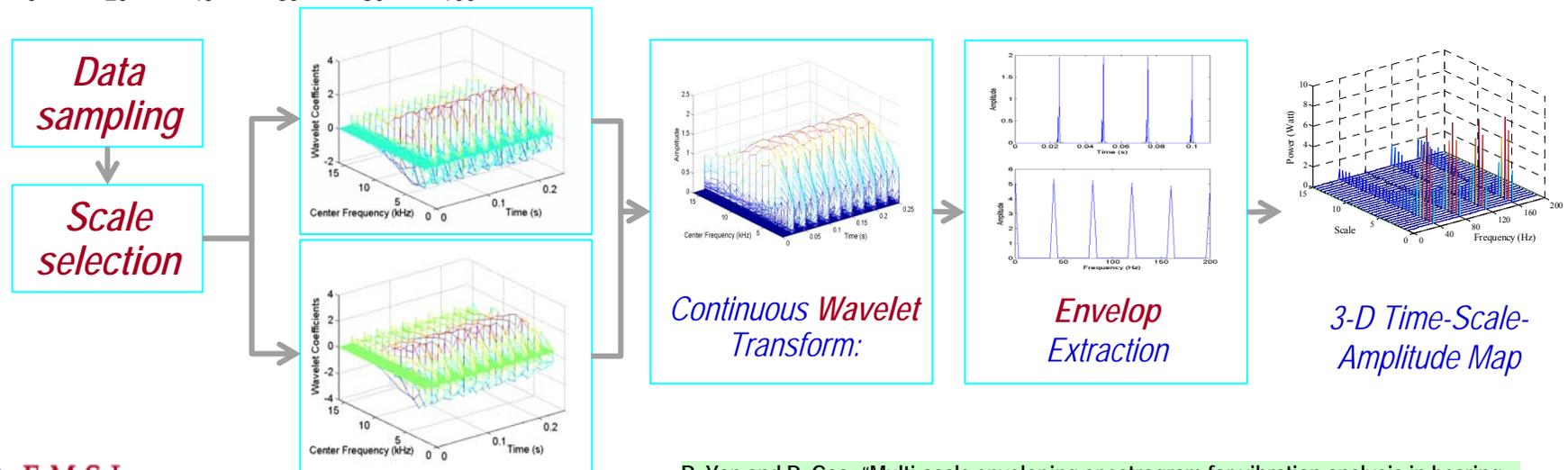
$$WT(s, \tau) = \frac{1}{\sqrt{s}} \int x(t) W^* \left( \frac{t - \tau}{s} \right) dt$$

Translation parameter:  
measure of time

Scale parameter

Mother template function

*Localized signature extraction through translating (shifting) and scaling of base wavelet functions*



EMSL

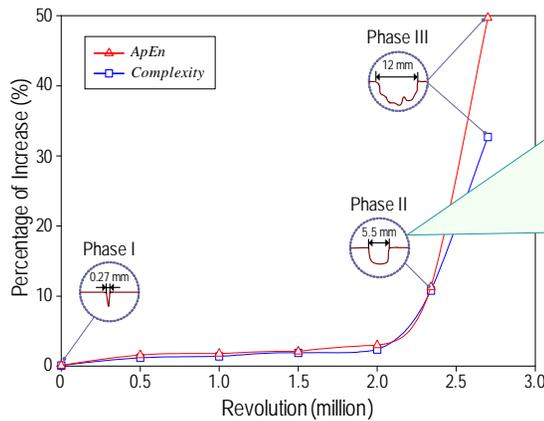
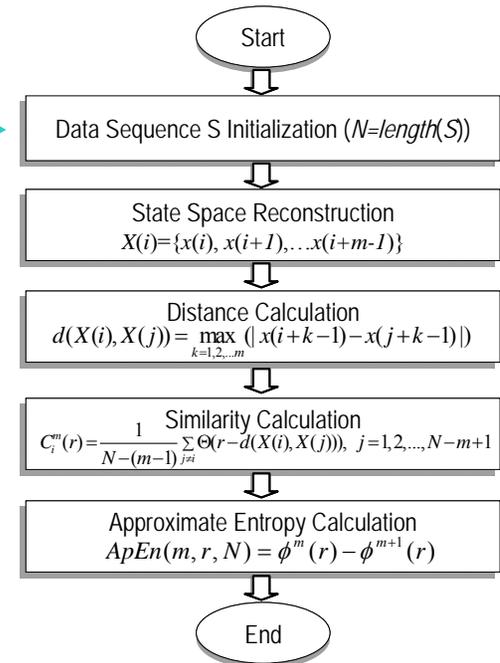
Electromechanical Systems Laboratory

R. Yan and R. Gao, "Multi-scale enveloping spectrogram for vibration analysis in bearing defect diagnosis", *Tribology International*, Vol. 42, No. 2, pp. 293-302, February, 2009.

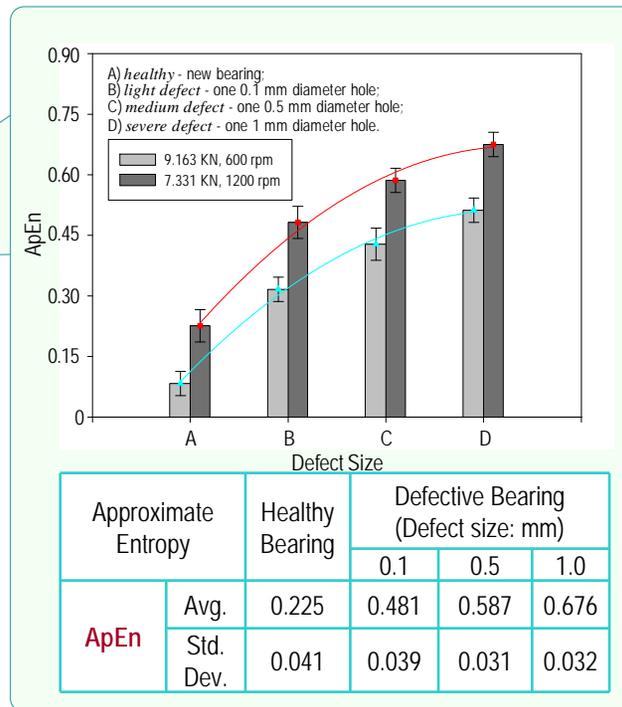
# Non-Linearity Measures

## Approximate Entropy (ApEn)

Definition:  $ApEn(m, r, N) = \phi^m(r) - \phi^{m+1}(r)$



Phase	Defect Size (mm)	ApEn	
		Avg.	Percentage of Increase
I	0.27	0.374	11.2%
II	5.50	0.416	49.7%
III	12.00	0.560	



- **Deterioration** of machine component (e.g. bearing) can be effectively identified by means of the **ApEn** values;
- **Efficient** computation (0.75 second /1,000 data points) enables **ApEn** for on-line applications.



EMSL

Electromechanical Systems Laboratory

R. Yan and R. Gao, "Approximate entropy as a diagnostic tool for machine health monitoring", *Mechanical Systems and Signal Processing*, Vol. 21, No. 2, pp. 824-839, 2007.

# Distributed Sensing

- Sensing Surface Mapping:
  - Distributed sensing
  - Continuous mapping based on discrete data
- Issues:
  - Surface techniques (TPS, sub-division, etc.)
  - Quality control in surface forming by regulating force distributions

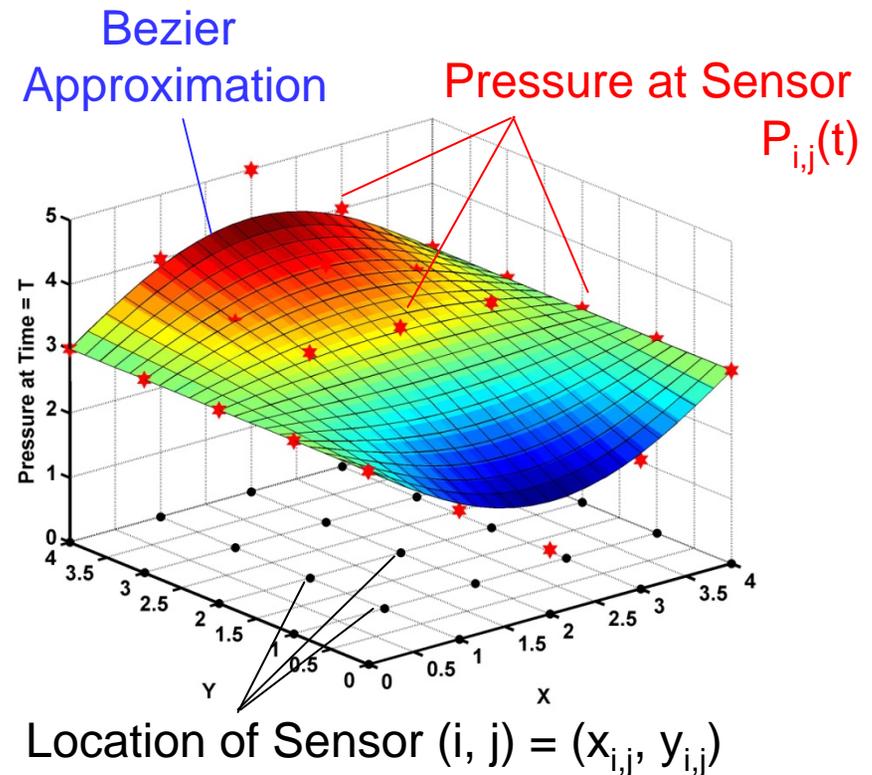
$$P(u, w, t) = \sum_{i=0}^n \sum_{j=0}^m B_{i,j}(t) J_{n,i}(u) K_{m,j}(w)$$

$$B_{i,j}(t) = \begin{bmatrix} x_{i,j} & y_{i,j} & P_{i,j}(t) \end{bmatrix}$$

$$J_{n,i}(u) = \binom{n}{i} u^i (1-u)^{n-i}$$

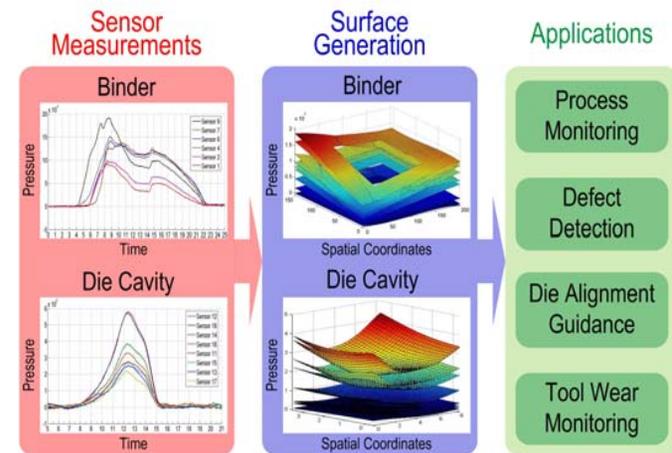
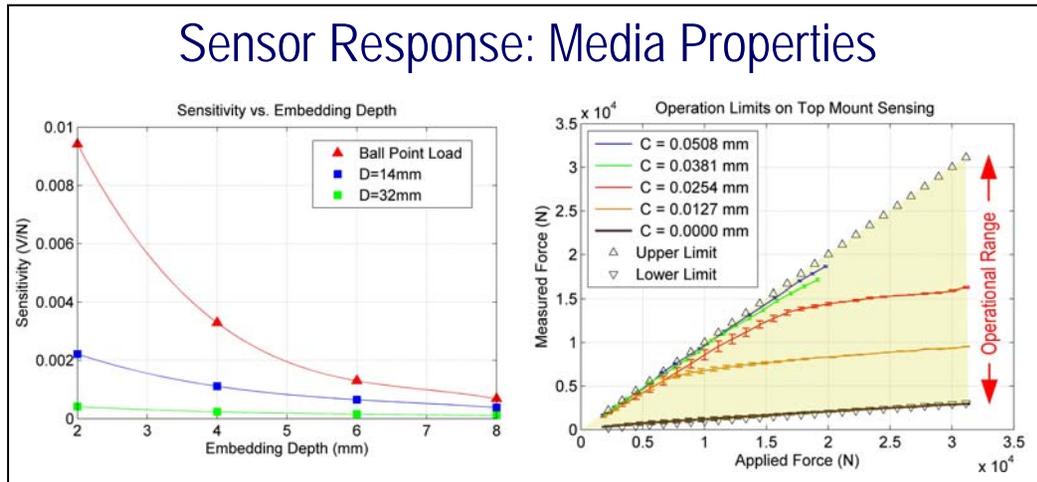
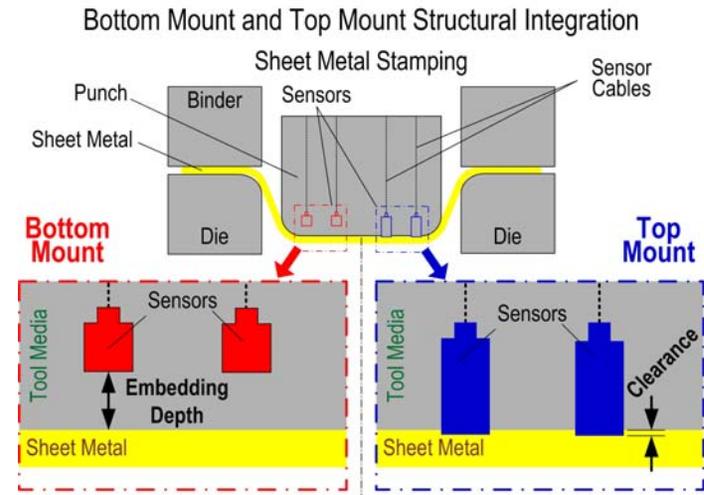
$$K_{m,j}(w) = \binom{m}{j} w^j (1-w)^{m-j}$$

$n, m$ : number of sensors - 1  
 $u, w$ : surface parameters



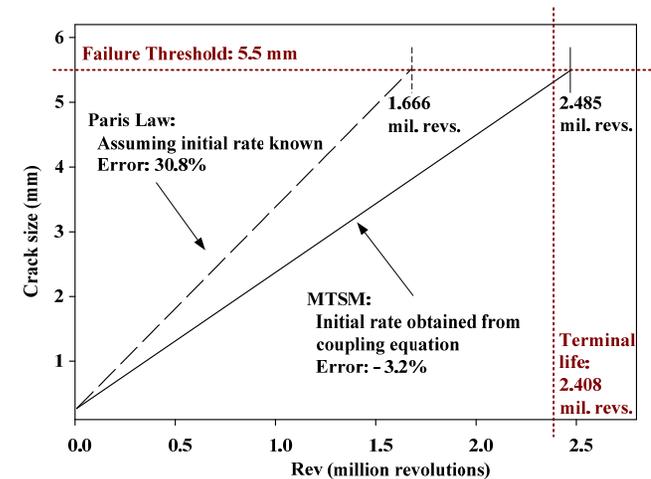
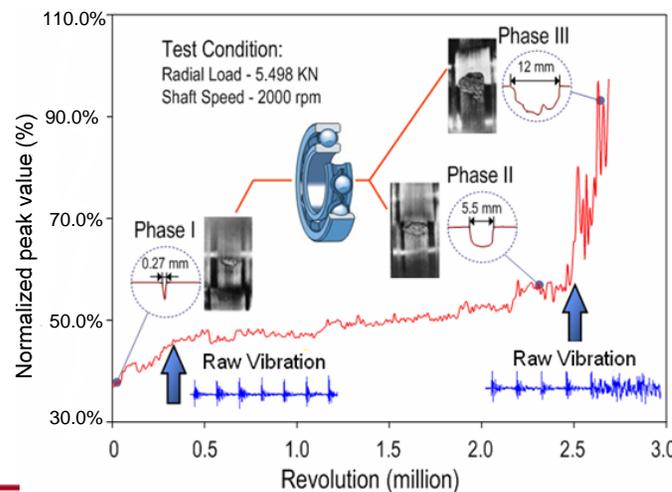
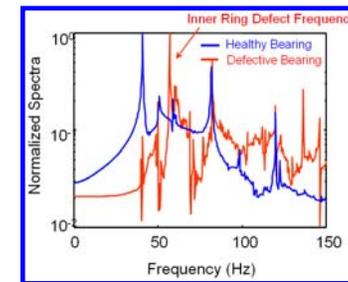
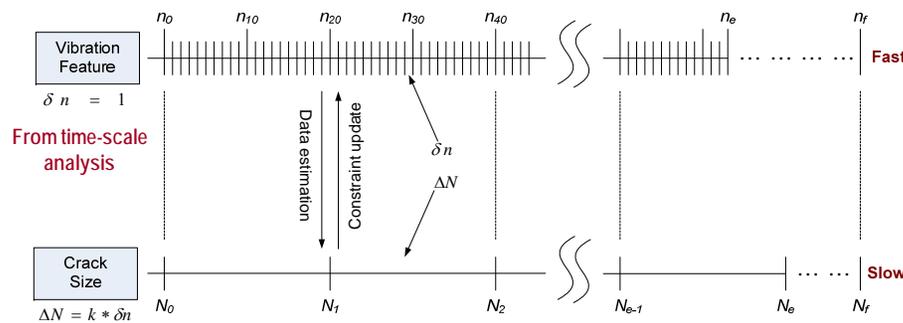
# Sensor Structural Integration

- Motivation:
  - Integrating sensors in manufacturing tools with functional *contact surfaces* facilitates *alignment control* sans deformation or stresses
- Issues
  - Sensor integration techniques
    - Top mount (Clearance)
    - Bottom Mount (Embedding depth)
  - Sensor-media interaction: *non-linear behavior*



# Prognosis of Defect Propagation

- To improve the accuracy of remaining service life prediction by combining the strength of empirical and physical models, based on the concept of Multi-time Scale Modeling (MTSM).
- Example: Improved prediction of remaining life of a rolling bearing
  - ✓ RNN-based prognosis: prediction of approximately 1.4 hours ahead;
  - ✓ MTSM-based prognosis: prediction of approximately 18.6 hours ahead.



# Summary

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- Sensing is critical to improved **observability** in nano-scale manufacturing
- Research needed for new, physics-based sensing **methodologies** to address challenges in the nano-domain:
  - ✓ **Self-energized, multi-modal, wireless**
    - Energy *harvesting* from process being measured
    - *Acoustic* and RF as information transmission media
    - Energy-efficient *coding* schemes
  - ✓ **Wavelets for surface metrology with nano-scale resolution**
    - Image denoising and surface filtering/reconstruction
    - Morphological feature extraction for localized stress/load assessment
    - Selection of best-suited wavelet, based on energy/entropy ratio
  - ✓ **Prognostics**
    - **M**ulti **T**ime **S**cale **M**odeling
    - Feature classification/reduction methods



# Acknowledgment

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- **National Science Foundation**

- Grants CMMI-0620957, 0428366, 0330171 ...

- **Collaborations**

- D. Kazmer (UMass Lowell)
- J. Cao (Northwestern)
- A. Deshmukh (Texas A&M)
- W. Gong (UMass Amherst)
- Former and present students ...



# Planning and control issues in nano-manufacturing



*Richard A. Wysk*

*Leonhard Chair in Engineering*

Industrial and Manufacturing Engineering

The Pennsylvania State University

# AGENDA

- Brief introduction to my limited nano involvement
- Problems with nano processes
- Illustrations
- Conclusions



# Potential Applications of Nano-sized Holes: Single DNA Detection

## Detecting Single Stranded DNA with a Solid State Nanopore

Daniel Fologea

*Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701*

Marc Gershow

*Department of Physics, Harvard University, Cambridge, Massachusetts 02138*

Bradley Ledden

*Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701*

David S. McNabb

*Department of Biological Sciences, University of Arkansas, Fayetteville, Arkansas 72701*

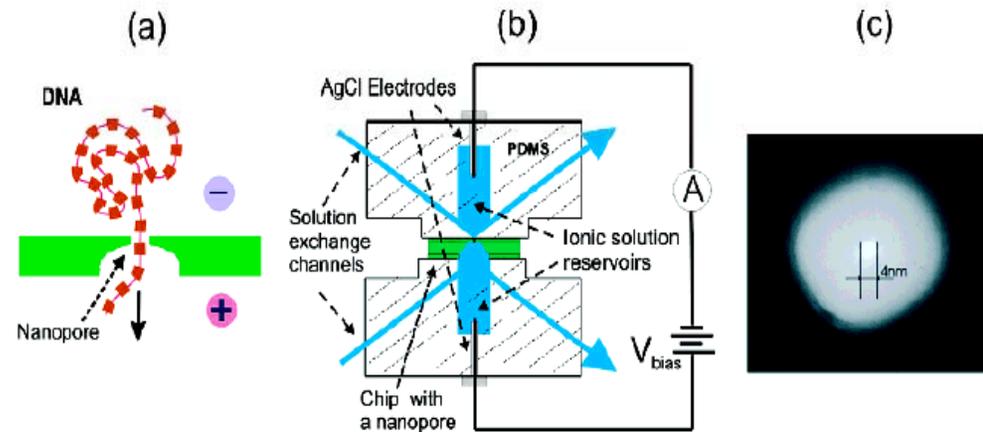
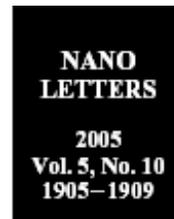
Jene A. Golovchenko

*Department of Physics, Harvard University, Cambridge, Massachusetts 02138 and  
Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138*

Jiali Li\*

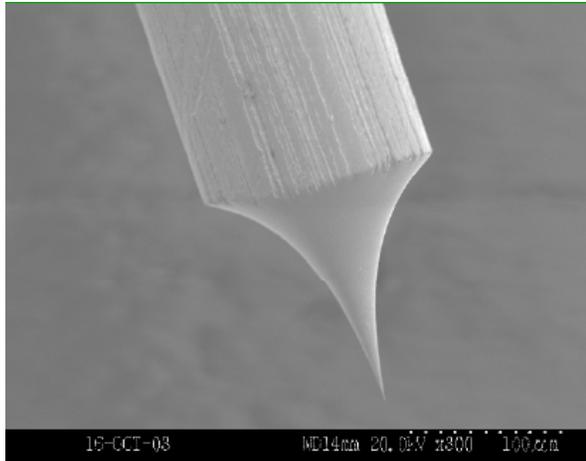
*Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701*

*Received June 24, 2006; Revised Manuscript Received August 15, 2006*

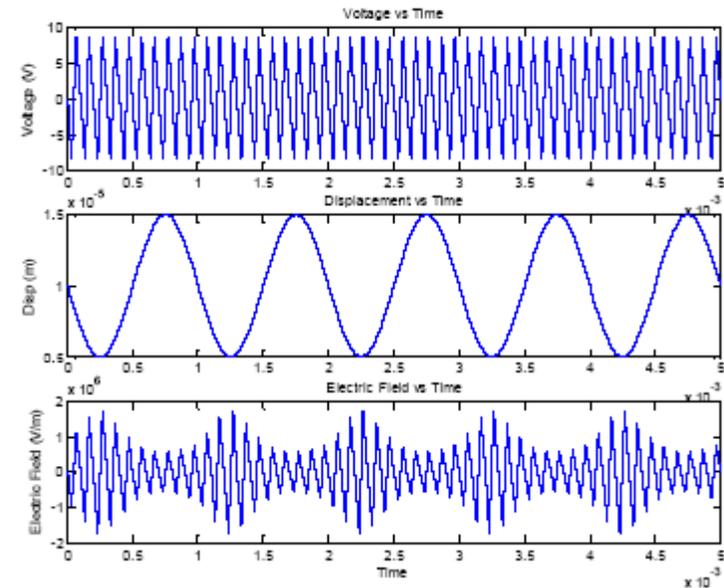
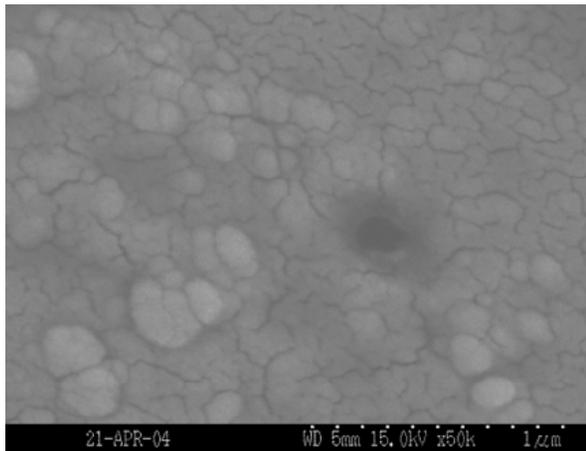


*Small holes (4nm) made by Focused Ion Beam*

# Related Research: nano-EM with STM Tip



Etched tungsten tip

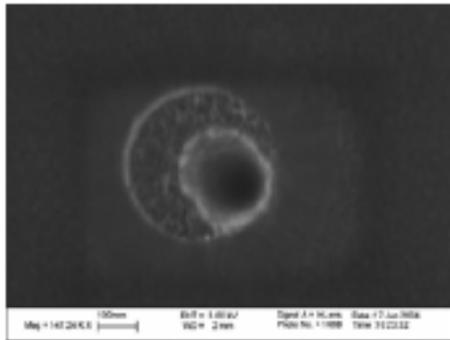


Distance modulation

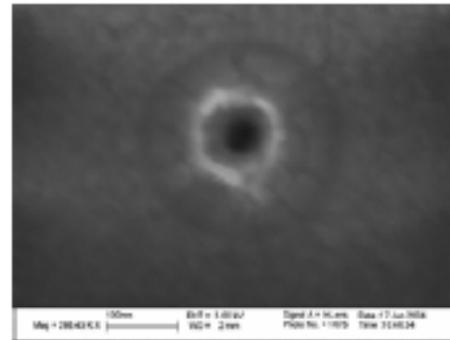
Resulting feature on Au (~ 200nm)

*U. of Kentucky (2004)*

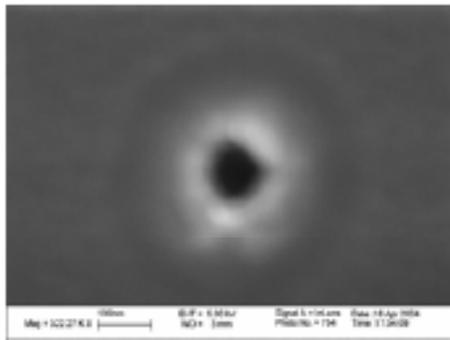
# Related Research: nano-EM with STM Tip (Cont'd)



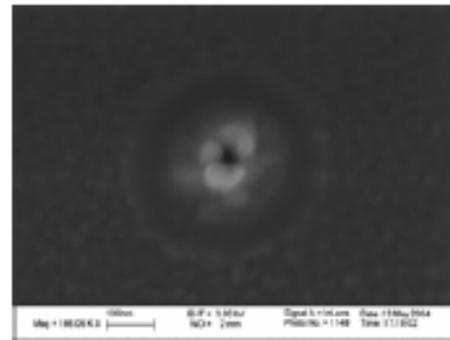
1nF-10V



1nF-6V



150pF-10V

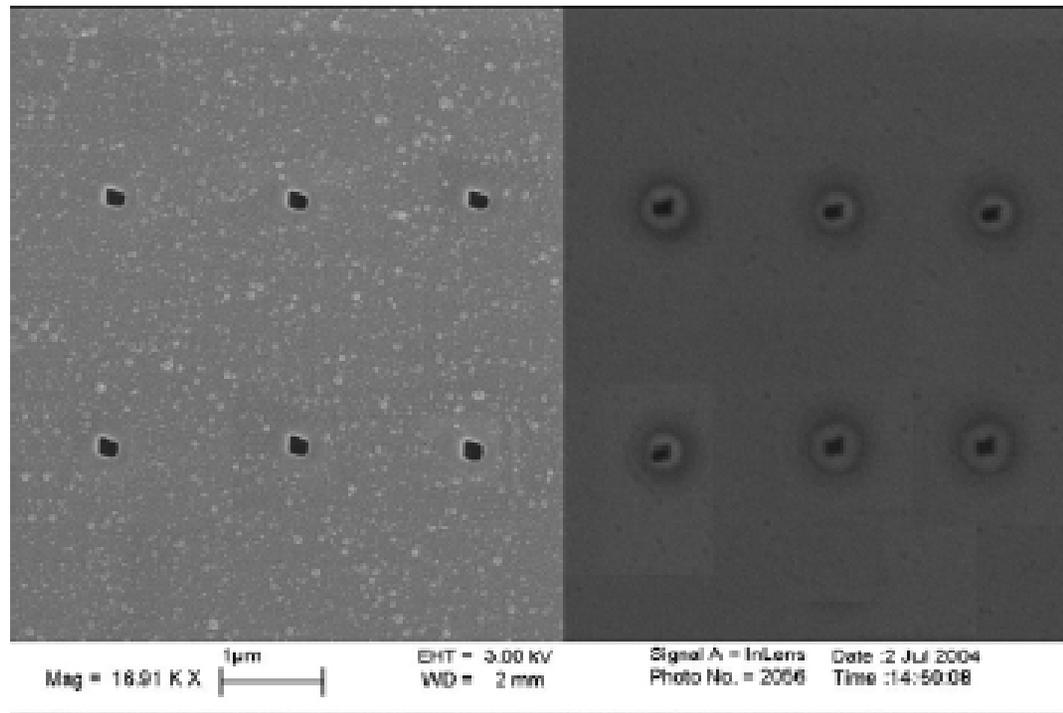


68pF-10V

Etched tungsten tip

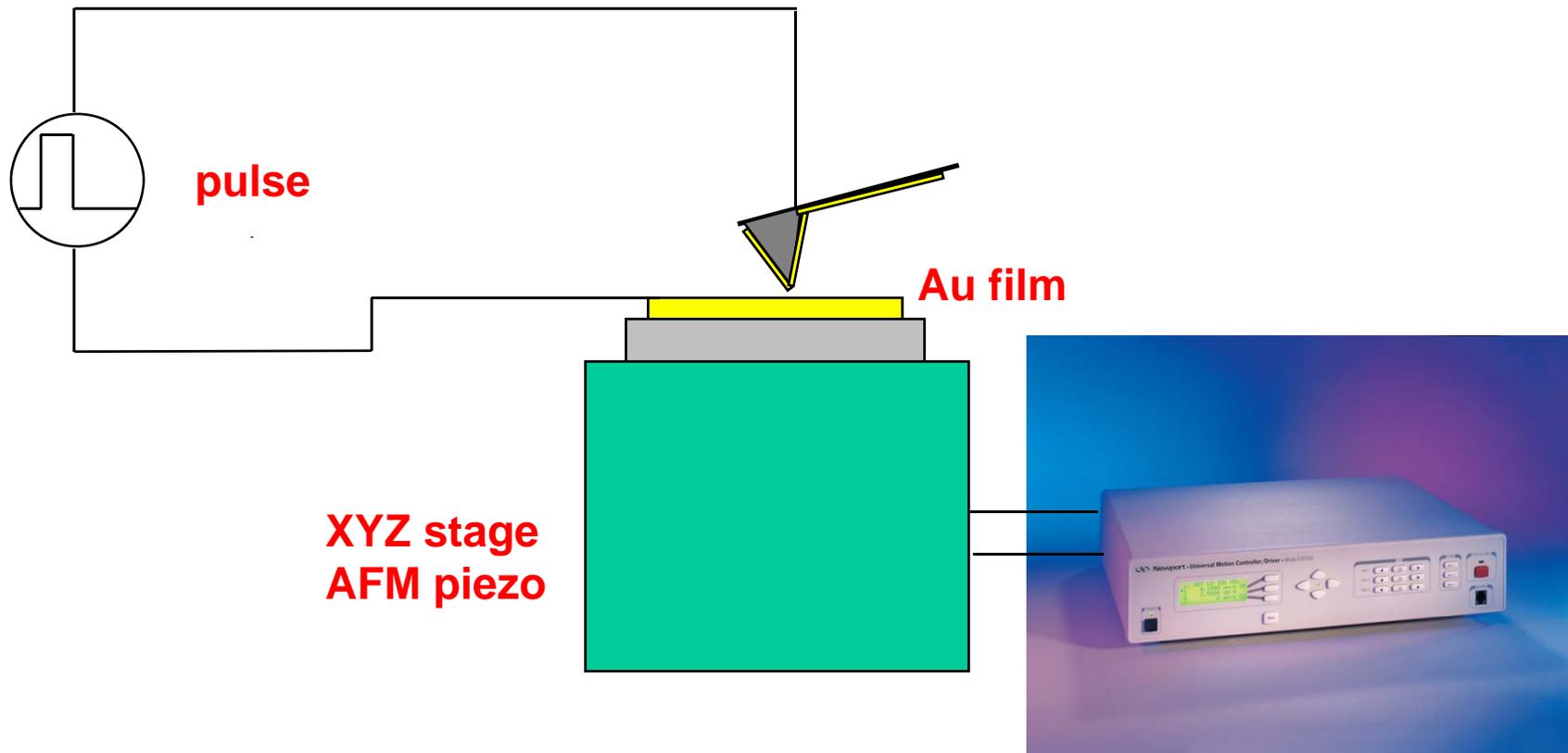
*U. of Maryland (2005)*

# Related Research: nano-EM with STM Tip (Cont'd)

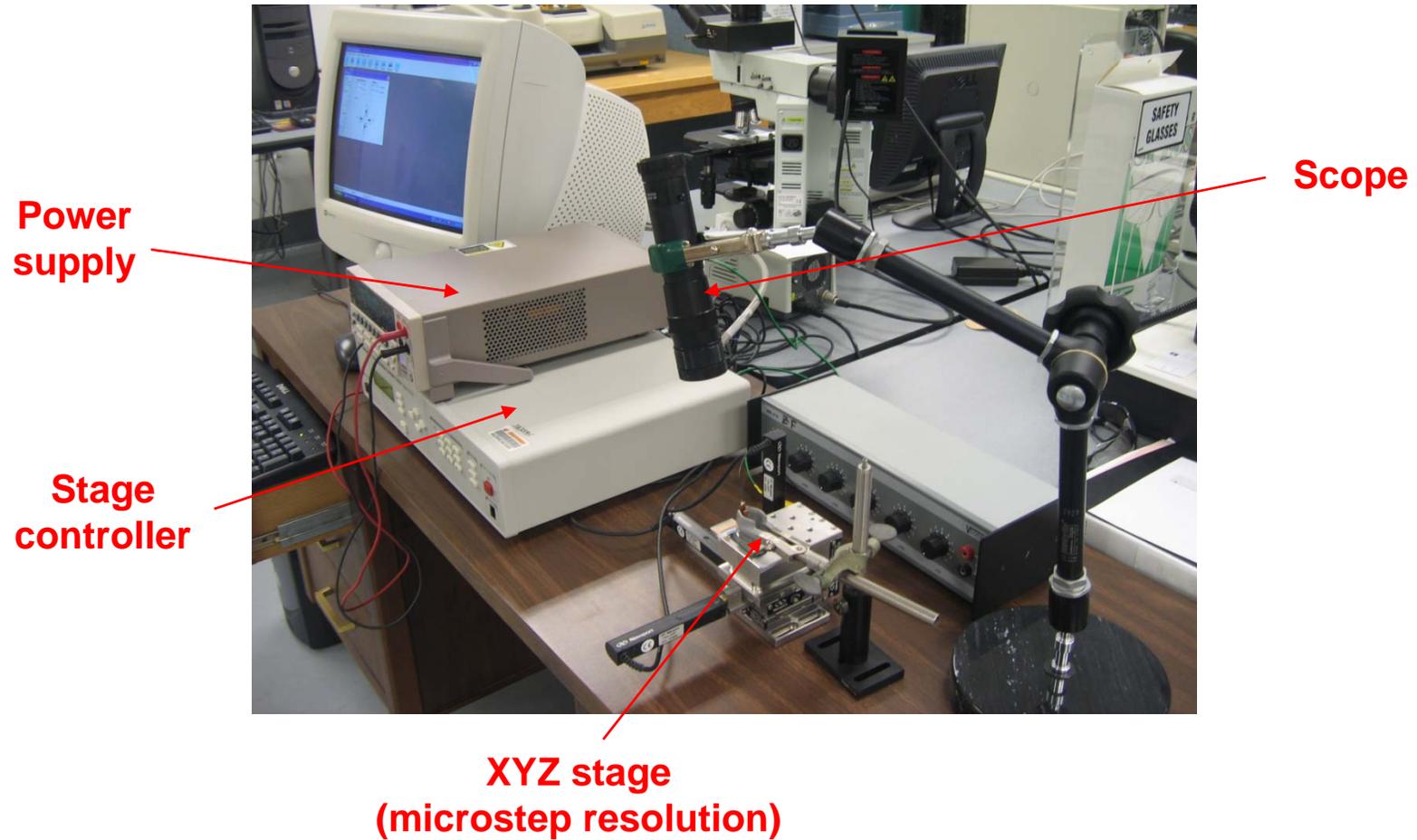


Front and back side images of Nano-drilled  
~150nm diameter holes on 30nm SiN membrane

# Nano-EM System Design



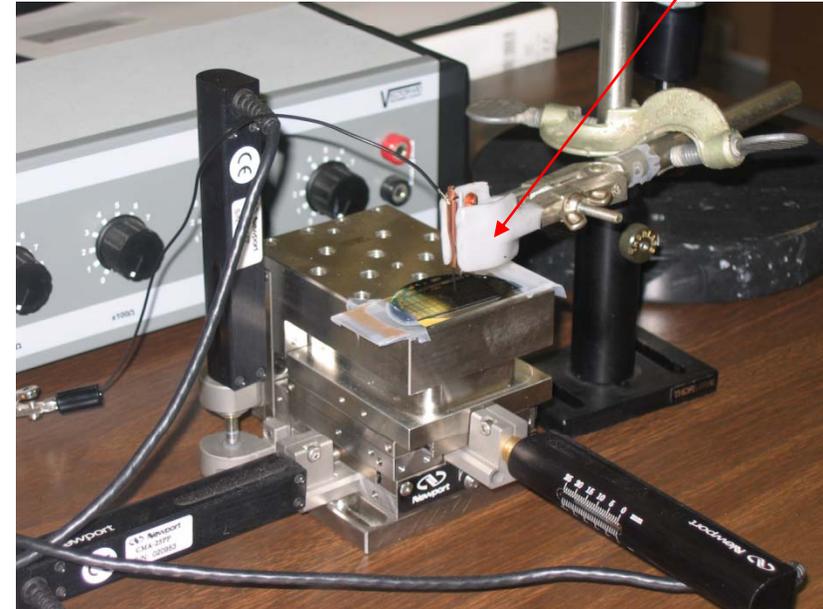
# Nano-EM Setup at FACCT



# Components of Nano-EM Setup



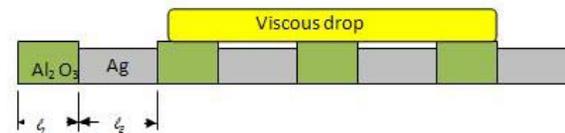
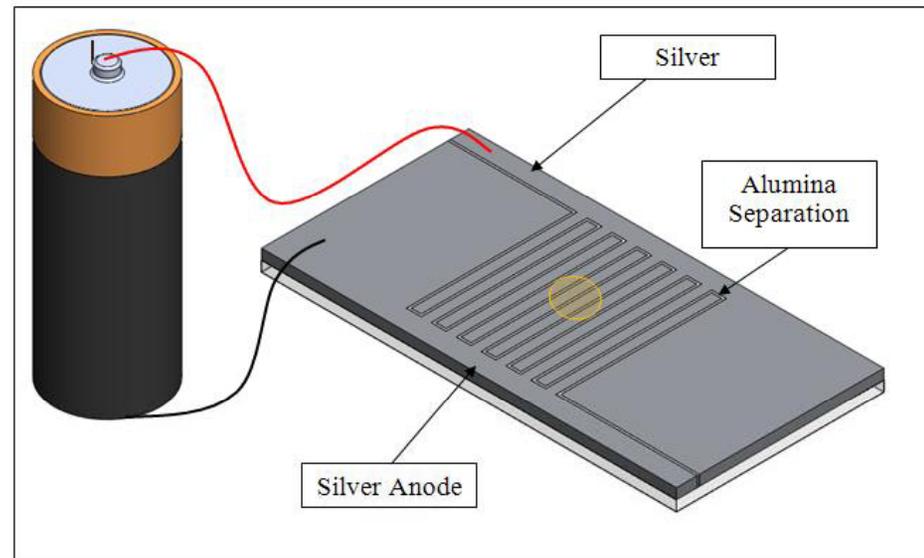
**Stage controller with feedback**



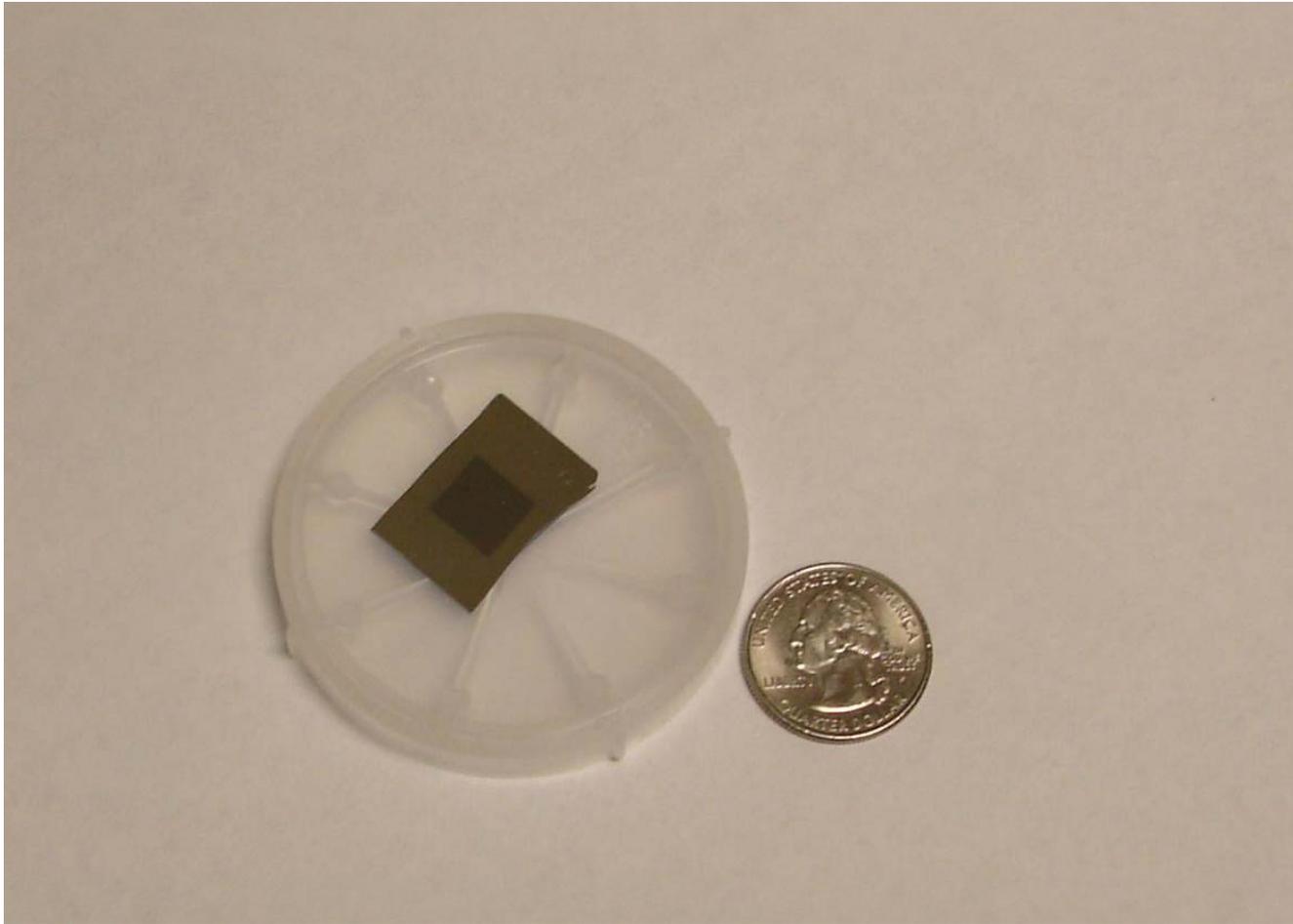
**XYZ stage  
(microstep resolution)**

# Medical Antiseptic Surface Applications

- *Creating medical quality devices*
- *Concept for a surface protection*



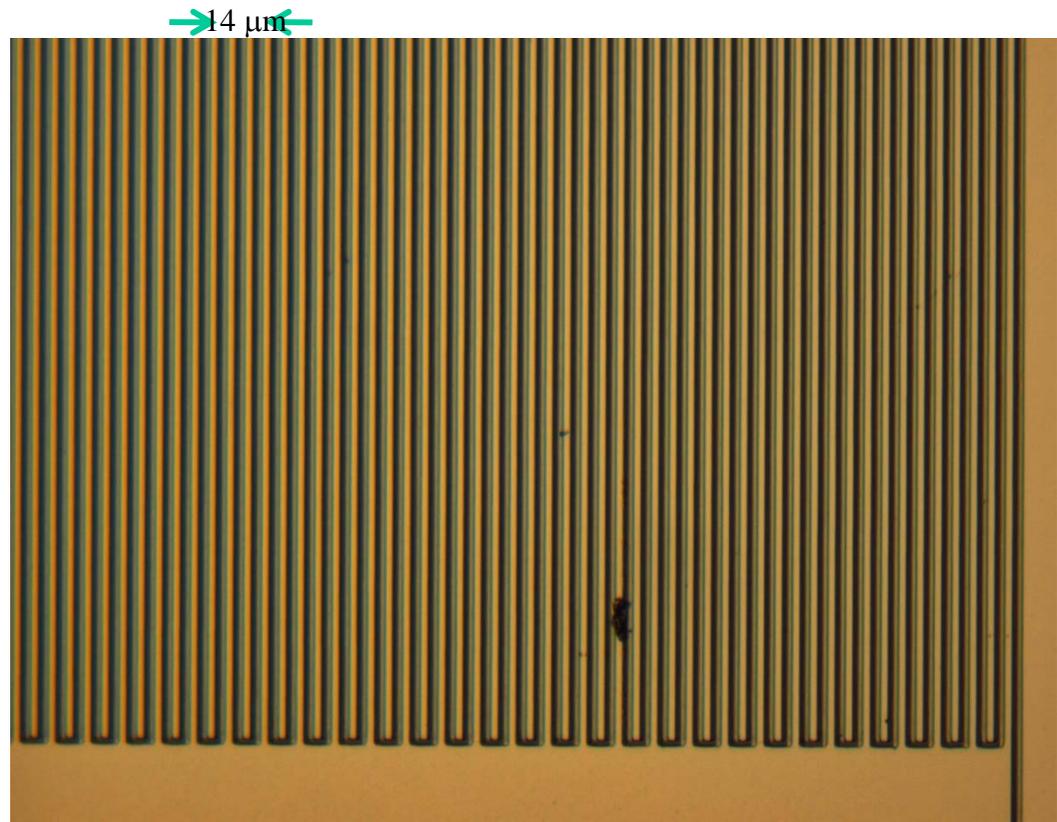
Our device at a very small scale



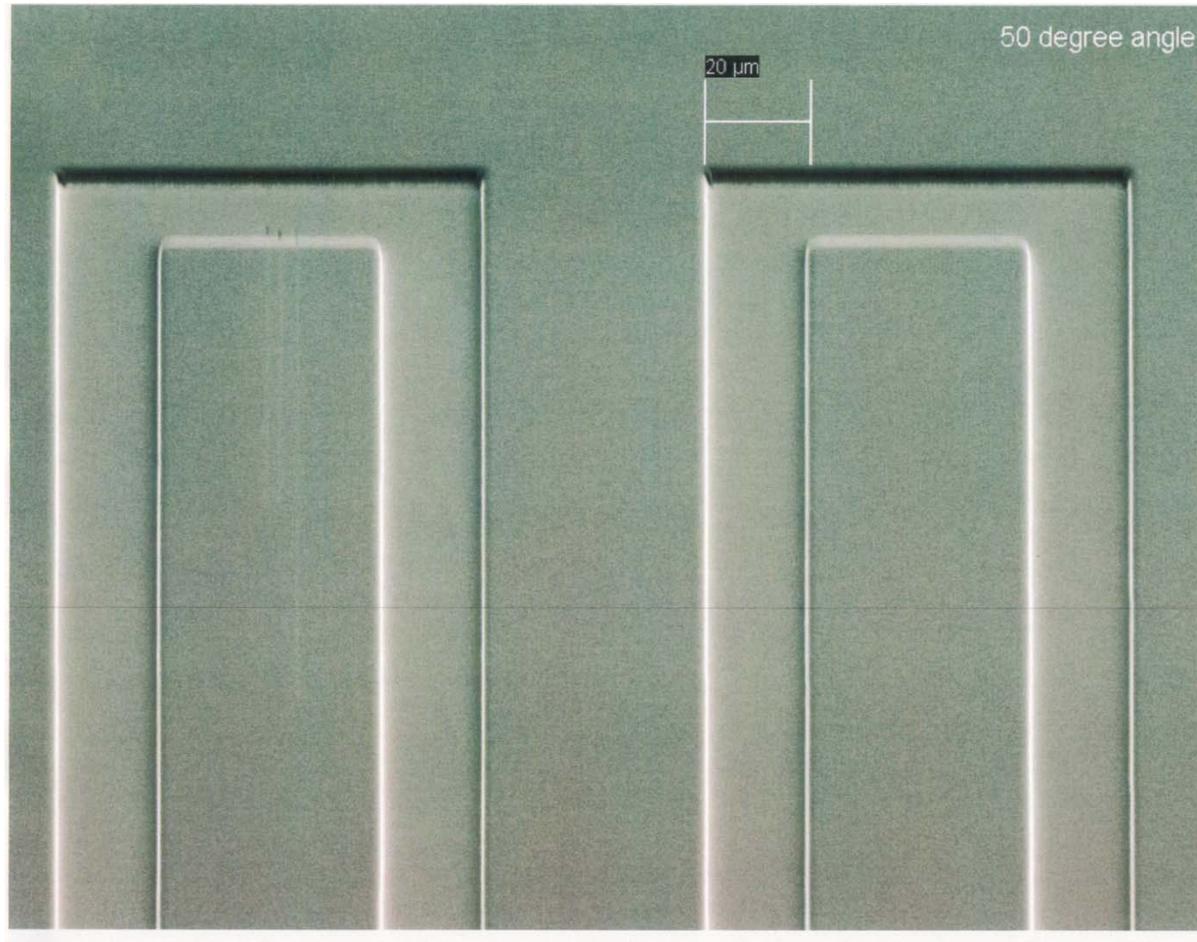
# Device characteristics

Small micro size samples 10 mm  
X 10mm  
2 size pathways  
6 $\mu$ m X 8 $\mu$ m and  
40  $\mu$ m X 20  $\mu$ m

The small sample as seen via an  
optical microscope



# SEM image of device



# Nano wires for medical applications

- 50 nm nano wires to be embedded within the body

# To digress before we begin

- Time and Cost to produce
- Need and then cost drive all of our engineering and manufacturing activities



# So what are the planning and control issues?

- Can we identify problems associated with planning and control of nano products?
- Can we relate these to other manufactured products?
- Are there methods and solutions?

# Economics



Product cost = engineering cost + materials cost + manufacturing cost

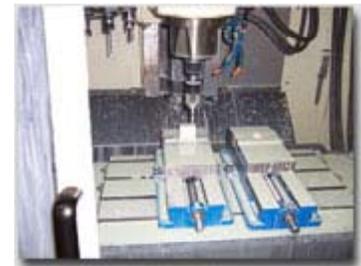
This is the cost for all parts that will be made and sold.

Product cost / part = engineering cost / total # of parts + materials cost / part + manufacturing cost / part

This is the cost for each part that will be made and sold.

# Engineering cost

- Product design ( $C_{ed}$ )
  - Cost of engineering design
- Process design ( $C_{pc}$ )
  - Cost of process planning
    - How is the part to be made
  - Cost of fixtures and tooling
- Production design ( $C_{pd}$ )
  - Cost of setting up production



# Material cost

- In most cases this is somewhat dependent of the number of parts
  - Economies of scale
  - Efficiencies of scale
- Additive or subtractive
  - Fractional or bulk materials



# Engineering cost

$$C_E = C_{ed} / n_t + C_{pc} / n_t + C_{pd} / n_b$$

total parts    total parts    parts in a batch



# Manufacturing cost

- One time costs
  - Process planning and design
  - Fixture engineering and fabrication
- Set up cost ( $C_{set}$ )
  - Cost to set up a process
- Processing cost ( $C_{psc}$ )
  - Cost of processing a part
- Production cost ( $C_{pdc}$ )
  - Cost of tooling and perishables



# Manufacturing cost

$$C_M = C_{\text{one}} / n_t + C_{\text{set}} / n_b + C_{\text{psc}} + C_{\text{pdc}} / n_{\text{tool}}$$

Total parts    parts in a batch    each part    tool cost by parts/tool



# So how can engineering and manufacturing costs be reduced for nano processing?



Machine cost



Fixture cost



Process planning cost

# Some observations on how can we make nano products more inexpensively?

- Large quantities of products
  - Little control here
- Set-up reduction
  - Make change-over and set-up very small
- Automation to reduce processing costs
- Start-up and quality issues
  - Identify critical components and dependencies for early processing

# Conclusions

- There are lots of opportunities for planning and control
- Some well know concepts can be used to focus effort into nano production
- Economy of scale issues
- Physics of size issues



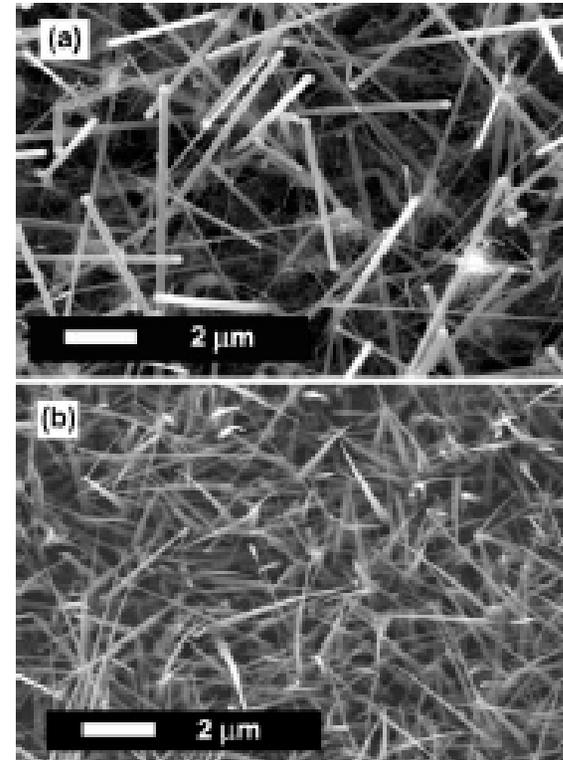
# STEP-AND-GROW APPROACH FOR PRECISELY POSITIONED NANOWIRE ARRAY STRUCTURE FABRICATION

*\*H. Carrion, \*S. Joshi, S. J. Fonash, W. J. Nam*

*\*Department of Industrial & Manufacturing Engineering  
Center for Nanotechnology Education & Utilization  
The Pennsylvania State University, University Park, PA 16802 USA*

# Technical Overview

- The **future success** of nanotechnology lies in the ability to **manufacture** in large volumes in an **economical** and **environmentally** sound manner.
- Over the past several years **considerable progress** has been made in the **synthesis** of nanoelements (powders, tubes, wires, rods, and fibers, among other geometries). However, **post growth assembly** techniques are **neither practical nor** necessarily **environmentally safe**.

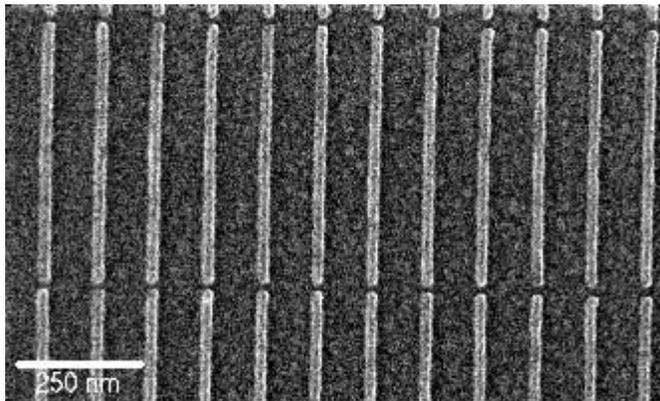
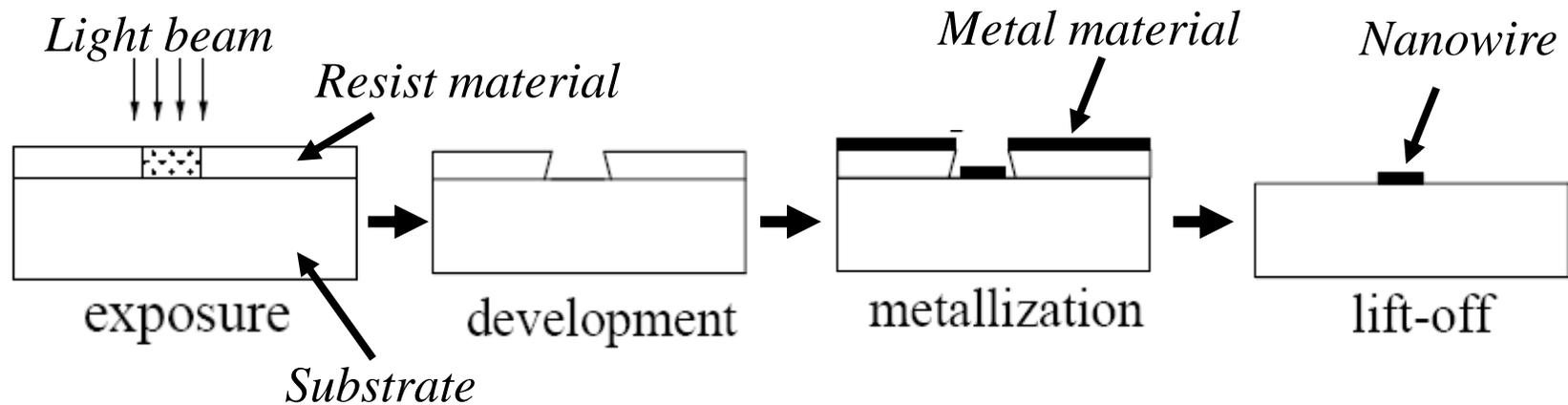


SiGe nanowires grown by VLS technique using a commercially available alumina template\*

\* Lew et al., Adv. Mater. Vol.15(24), pp. 2073

# Current Techniques (Synthesis)

## \* TOP-DOWN Approach Example



### ADVANTAGES:

- Highly oriented wires
- Good contact with electrical terminals

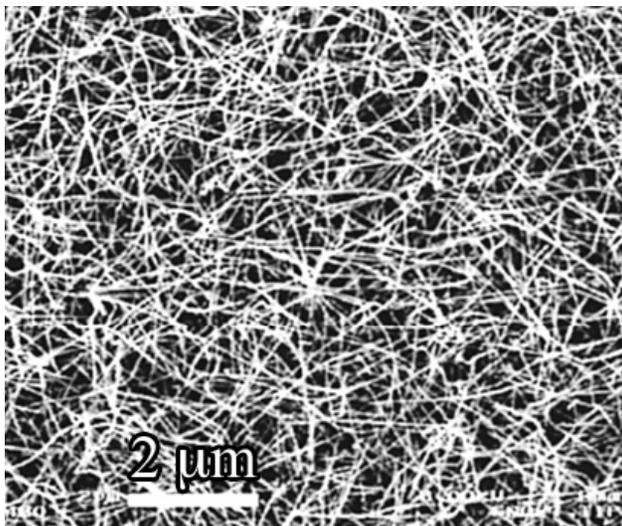
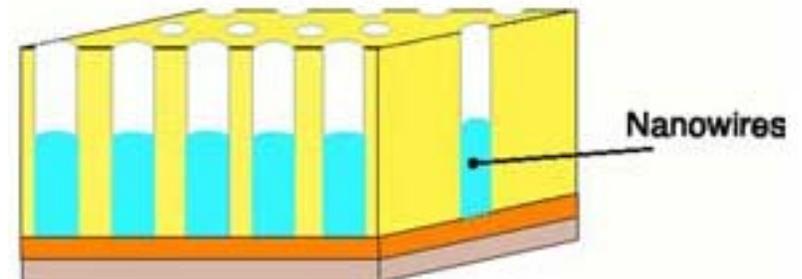
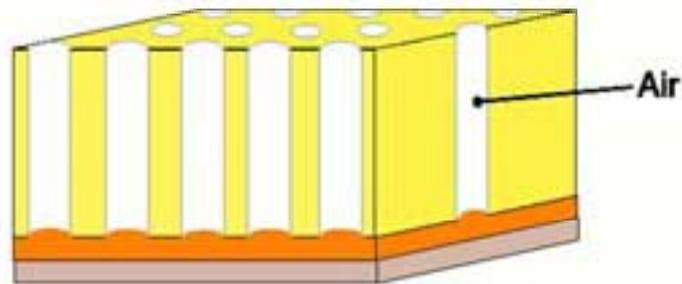
### DISADVANTAGES:

- Slow & expensive

# Current Techniques (Synthesis)

## \* BOTTOM-UP Approach Example

- Porous materials as host templates for nanowire growth
- Techniques for filling the templates: pressure injection, electrochemical deposition, vapor deposition



### ADVANTAGES:

- Cost effective

### DISADVANTAGES:

- Need to harvest
- Placement needed

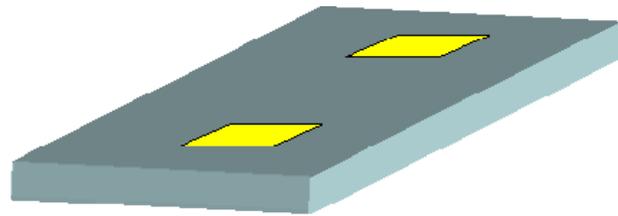
# Manufacturing Perspective

- Reduce Cost
- Reuseable “tooling”
- Establishing process parameters
- Process time, throughput
- Dimensional Specs
- In process Inspection
- Yield, Quality, Process Repeatability

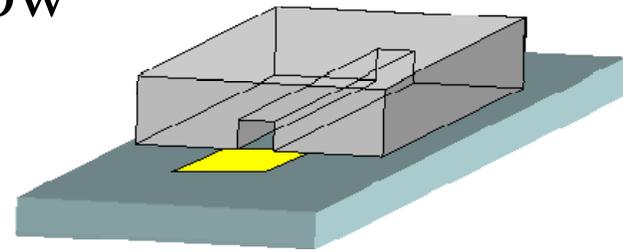
# Step-and-Grow Approach - Using the Reusable Template

Example: Polyaniline (PANI) Nanowire Synthesis

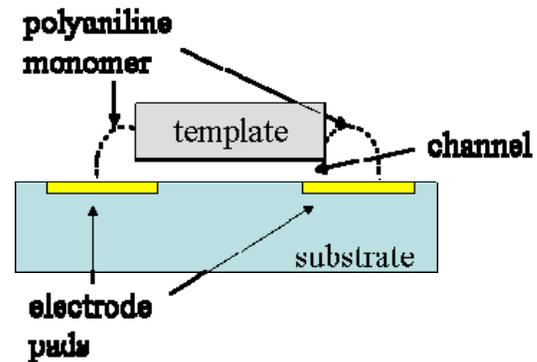
Process Flow



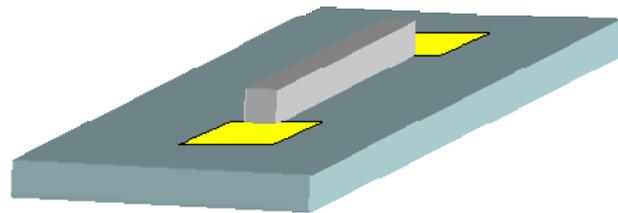
electrical pads on substrate



positioning of template

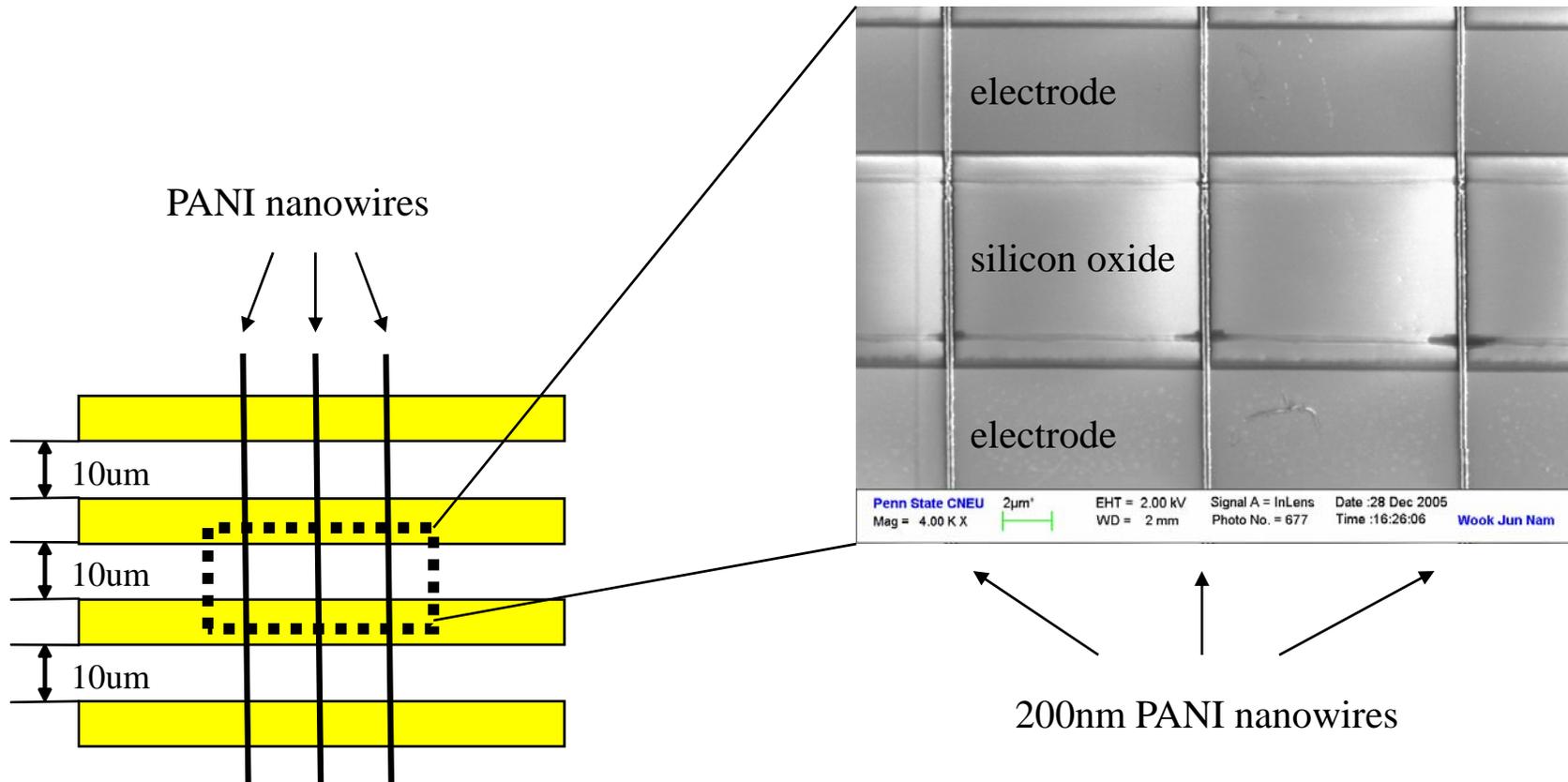


synthesis



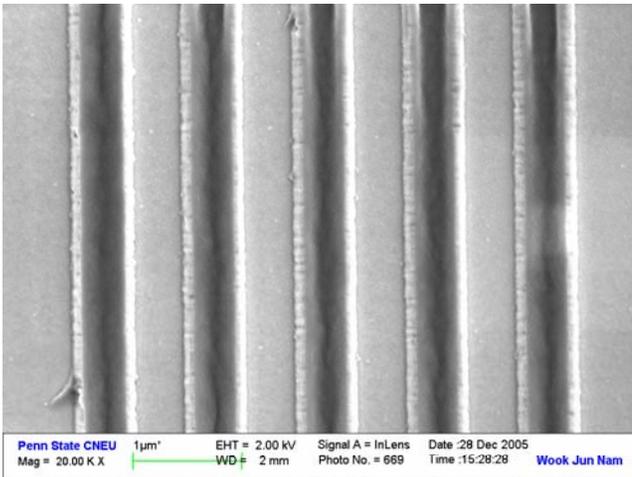
separation

# Synthesized PANI Nanowires

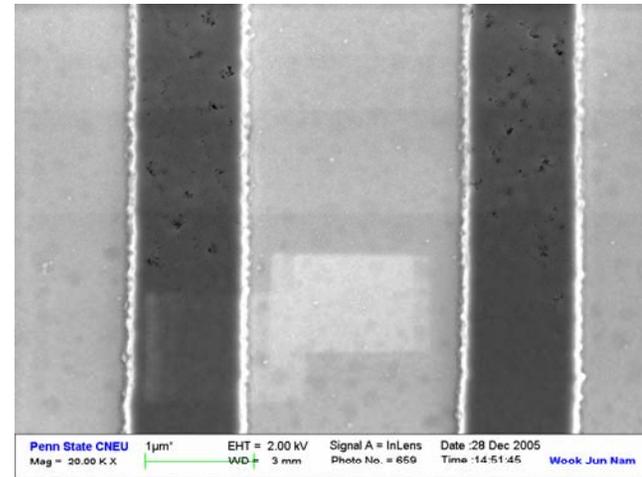


# Synthesized PANI Nanowires

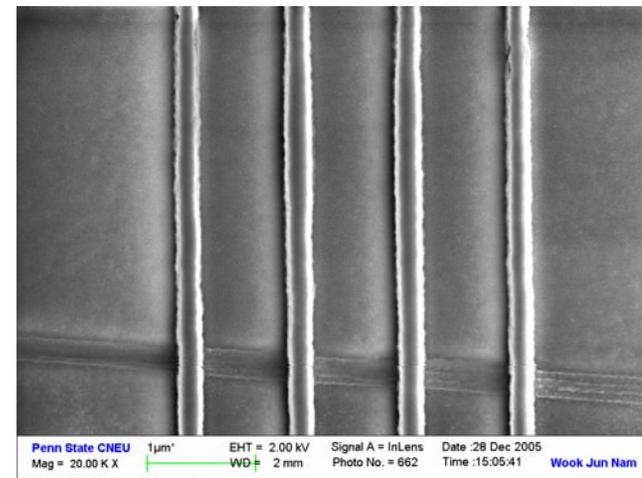
- Demonstration of 40 Sequential Synthesis Events Using a Single Template Plate



500nm

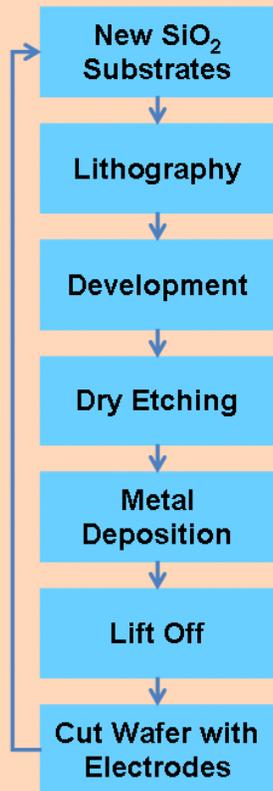


1μm

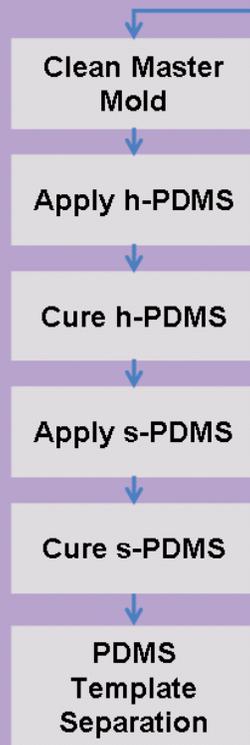


200nm

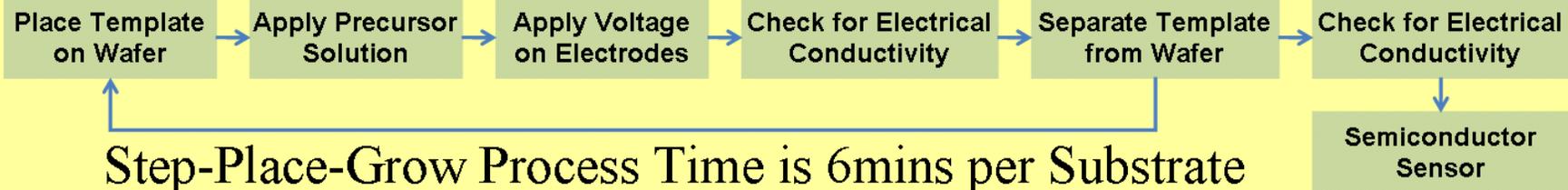
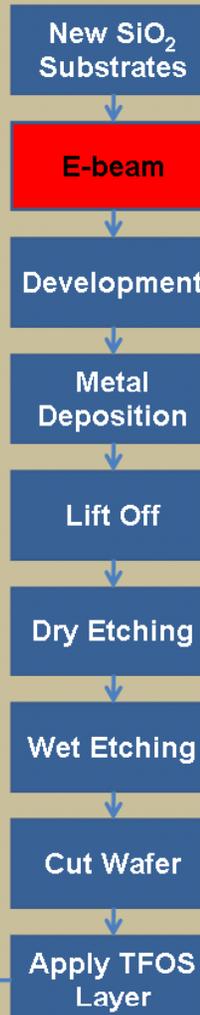
Fabrication of Electrodes  
Process time is 8hrs  
(Multiple Wafers)



Fabrication of Templates  
Process time is 3hrs  
(Multiple Templates)



Fabrication of Master Mold  
Process time is 1day  
(Only 1 Wafer!)



# Does scale matter in nanomanufacturing?

## - process design and control

November 3, 2009

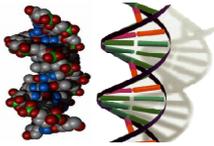
Prof. Sang-Gook Kim

Park Center for Complex Systems  
Massachusetts Institute of Technology

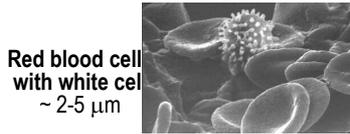
# Complexity at different scales

$10^{-9}$

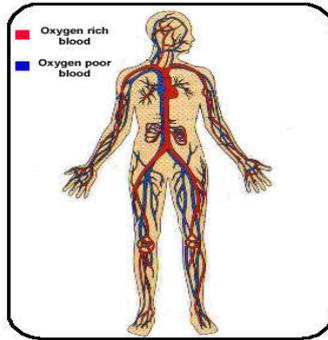
$10^3$



DNA  
~2-1/2 nm diameter



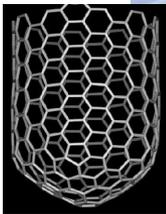
Red blood cell  
with white cell  
~ 2-5  $\mu\text{m}$



MIT Stata Center  
>\$300 million, 5 years

natural

manmade

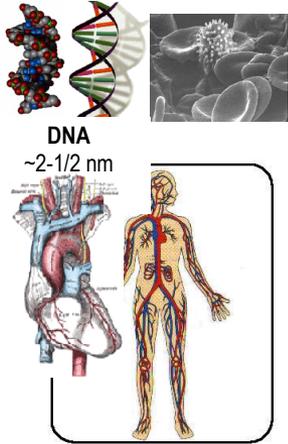


Carbon nanotube  
~2 nm diameter

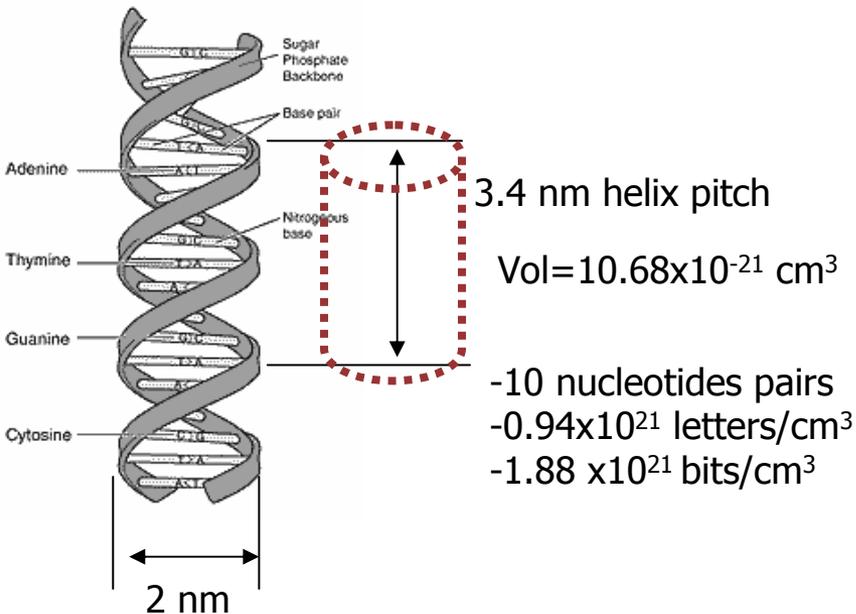


MIT Simmons Hall  
\$90 million, 2 years

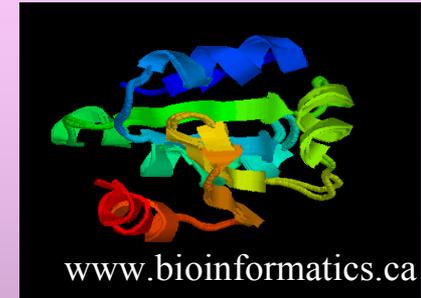
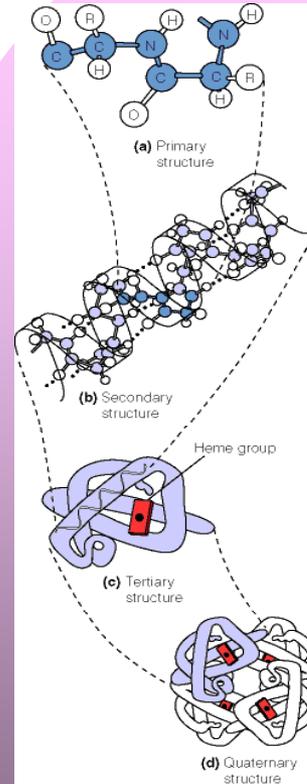
Natural



← More complex?



W. Gitt, J. Creation, V.10 (2), P 181, 1996



**Nanoscale Complexity**

- Solving Gaussian integrals or unlocking a combination lock

$$\int D\phi e^{i\int dt \frac{d\mathbf{x}}{dt}(t)^2}$$



- Understanding how proteins fold
- Assembling nanostructures deterministically
- Predicting Dow Jones index one year from today ?
- Planning an optimum US health care system
- Assembling individual CNTs deterministically over m<sup>2</sup> area?
- **What are the imperatives for planning and control in nanomanufacturing?**

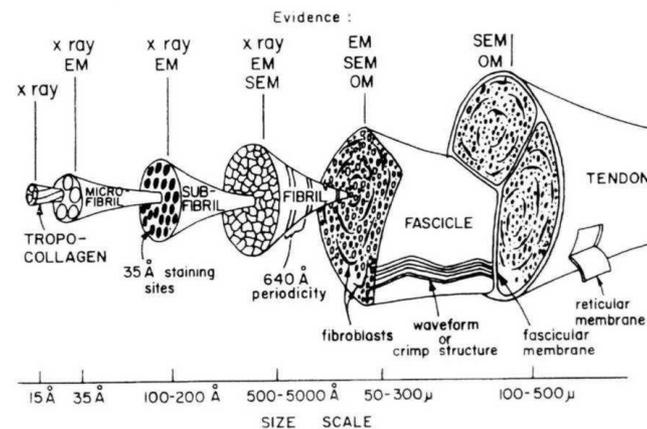
# How complexity can be reduced or minimized?

A system is complex when;

- A design is coupled.
- Coupling propagates through combinatorial manner
- The scale order is very high. (over  $10^9$ )
- System ranges vary with time. The outcome is uncertain. (low probability of success)

Complexity can be reduced by;

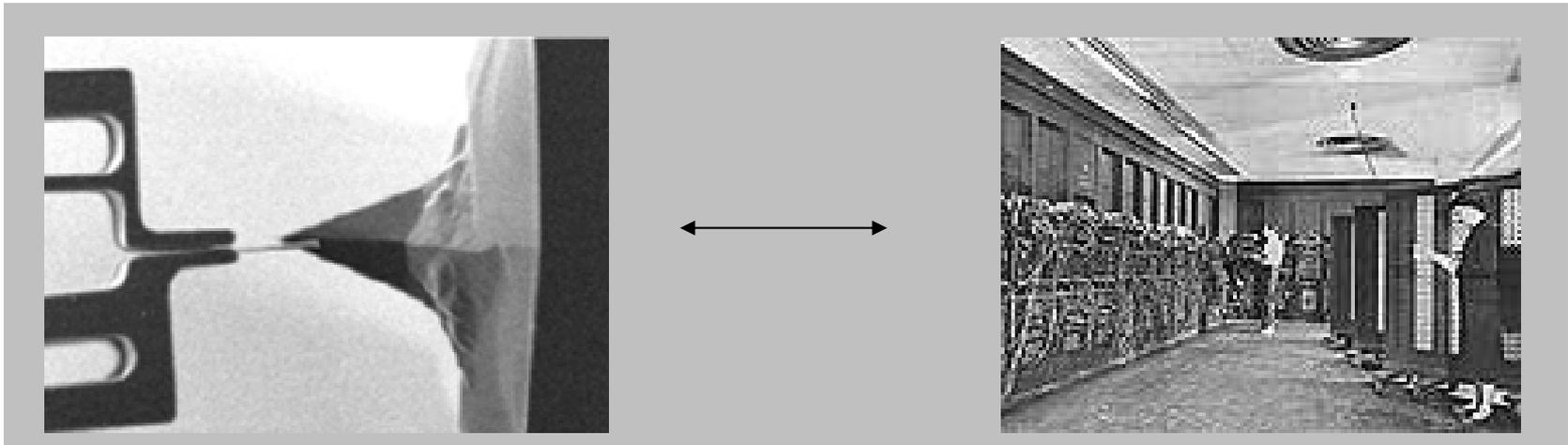
- Uncoupled design
- DPs with high probability of success
- Periodicity (temporal, spatial, etc.)
- Right process tool



By Prof. Nam Suh, MIT

# Nano Assembly:

## Design for Assembly at Micro and Nano Scales

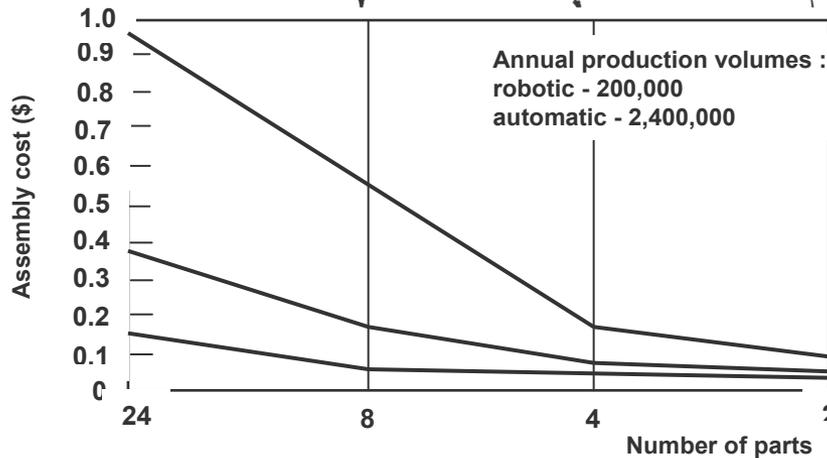
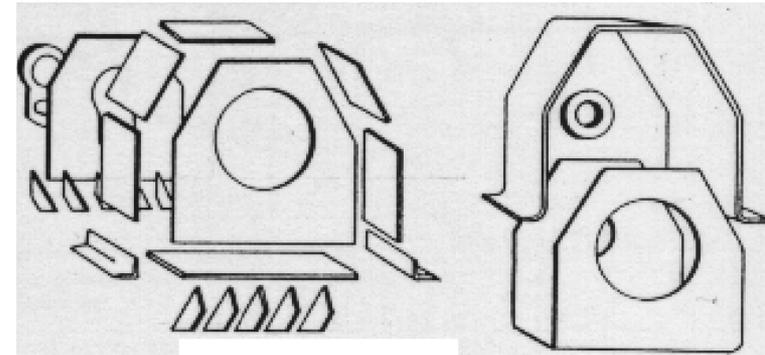
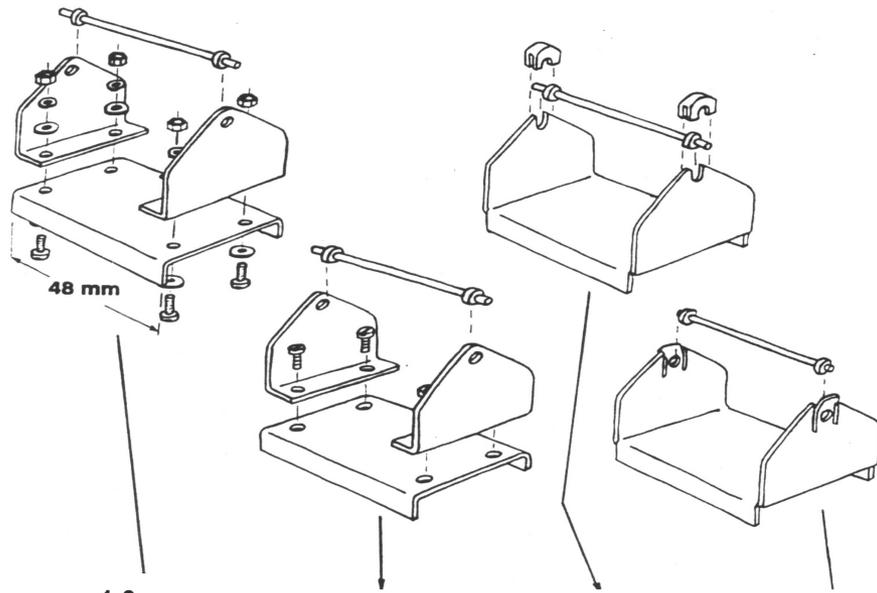


Direct CNT manipulation  
(Carlson et al, Nanotechnology, 2007)

ENIAC  
18,000 Tubes  
Debugging

## DFA - Example

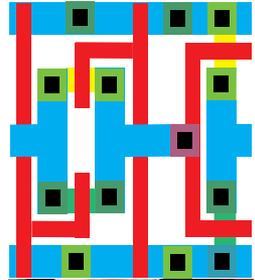
Minimize the number of parts



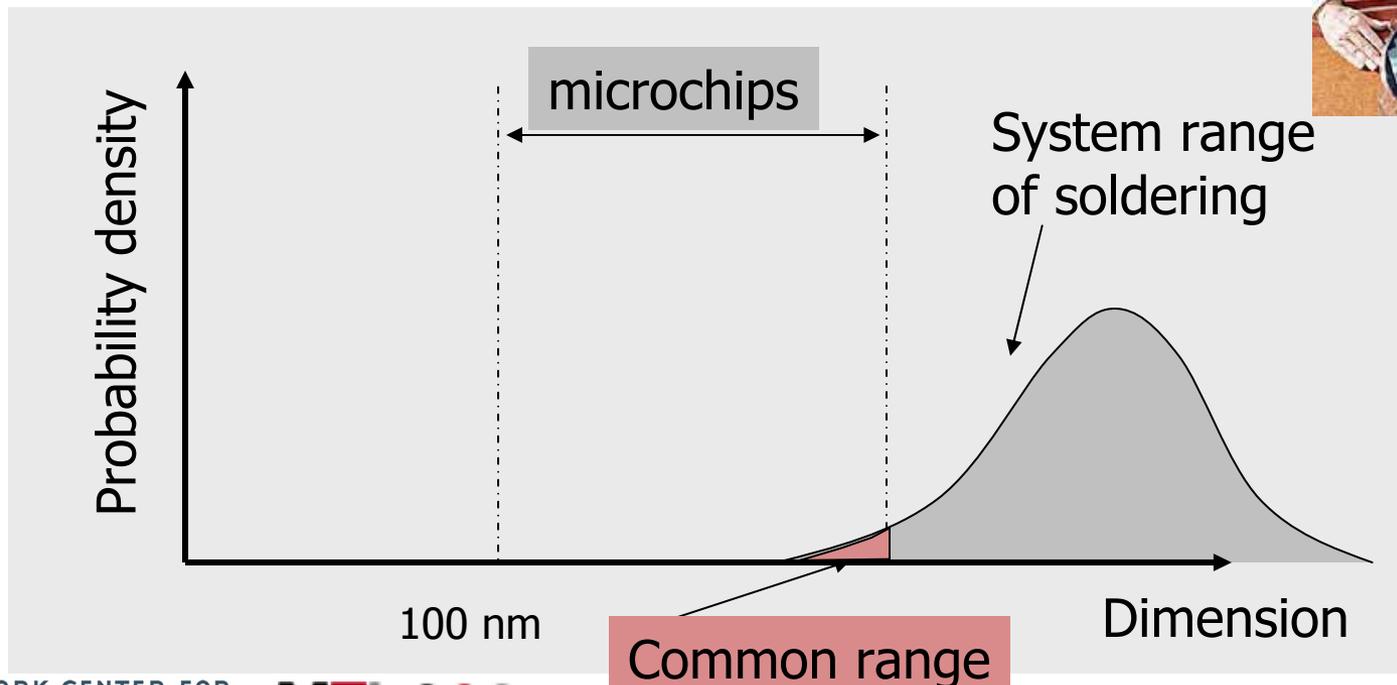
- Information Content
- Old assembly technology for microstructures
- **Tyranny of numbers**

**Probability of success = common range/system range**

## Monolithic Design

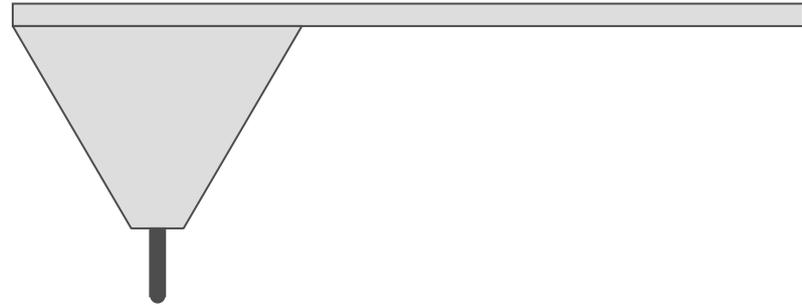


J. Kirby of TI (1958)  
R. Noyce, Intel (1959)

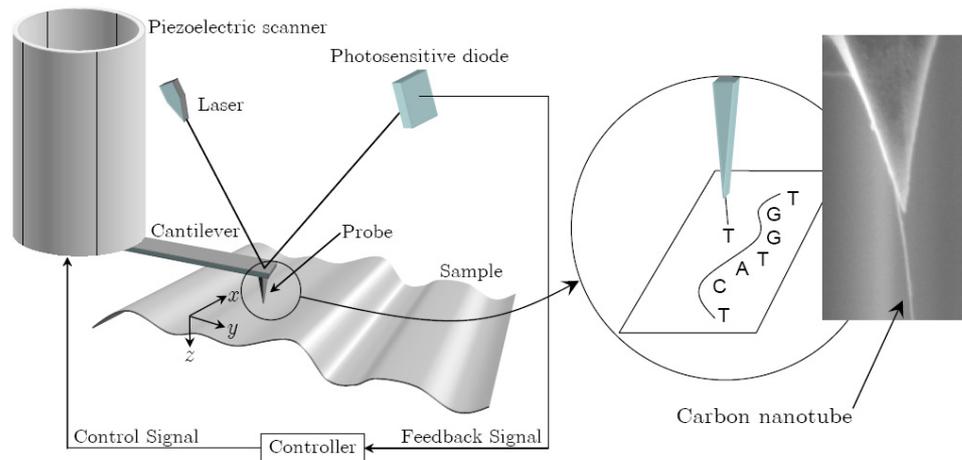


## Applications:

- Scanning probe
- Micro/nano manipulator
- Sensor
- CNT characterization tool



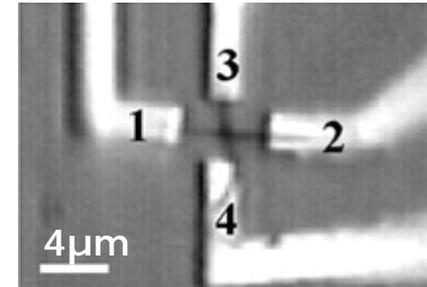
## Example: DNA sequencing



(Burn et al, ISNM 2006)

## Direct manipulation of nanostructures

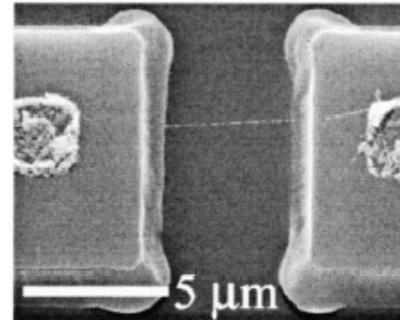
- Serial process (slow)
- Require expensive equipments



CNT-based nonvolatile RAM  
(Rueckes et al of Harvard, Science, 2000)

## Catalytic growth

- Large variations
- Limited flexibility and control

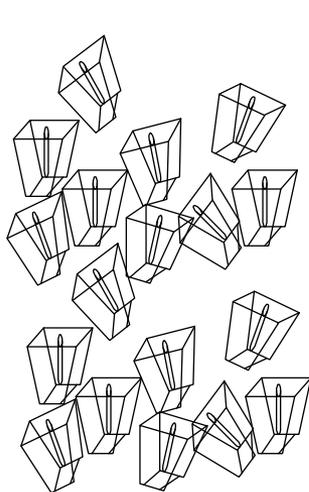
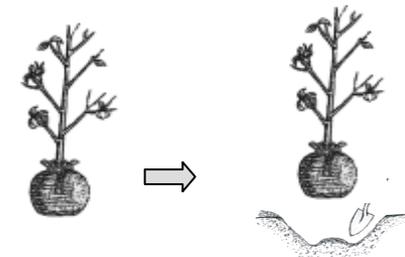
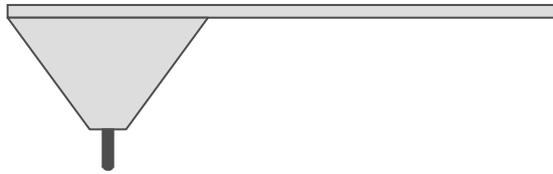


CNT interconnection  
through catalytic growth  
(Franklin et al, APL 81, 2002)

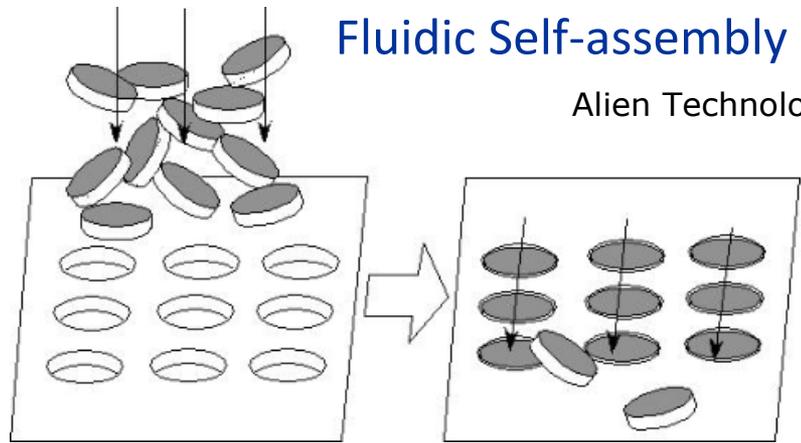
## (Artificial) self-assembly

- Difficult to handle the individual nanostructures
- Large variations

# Transplanting Assembly – a new concept



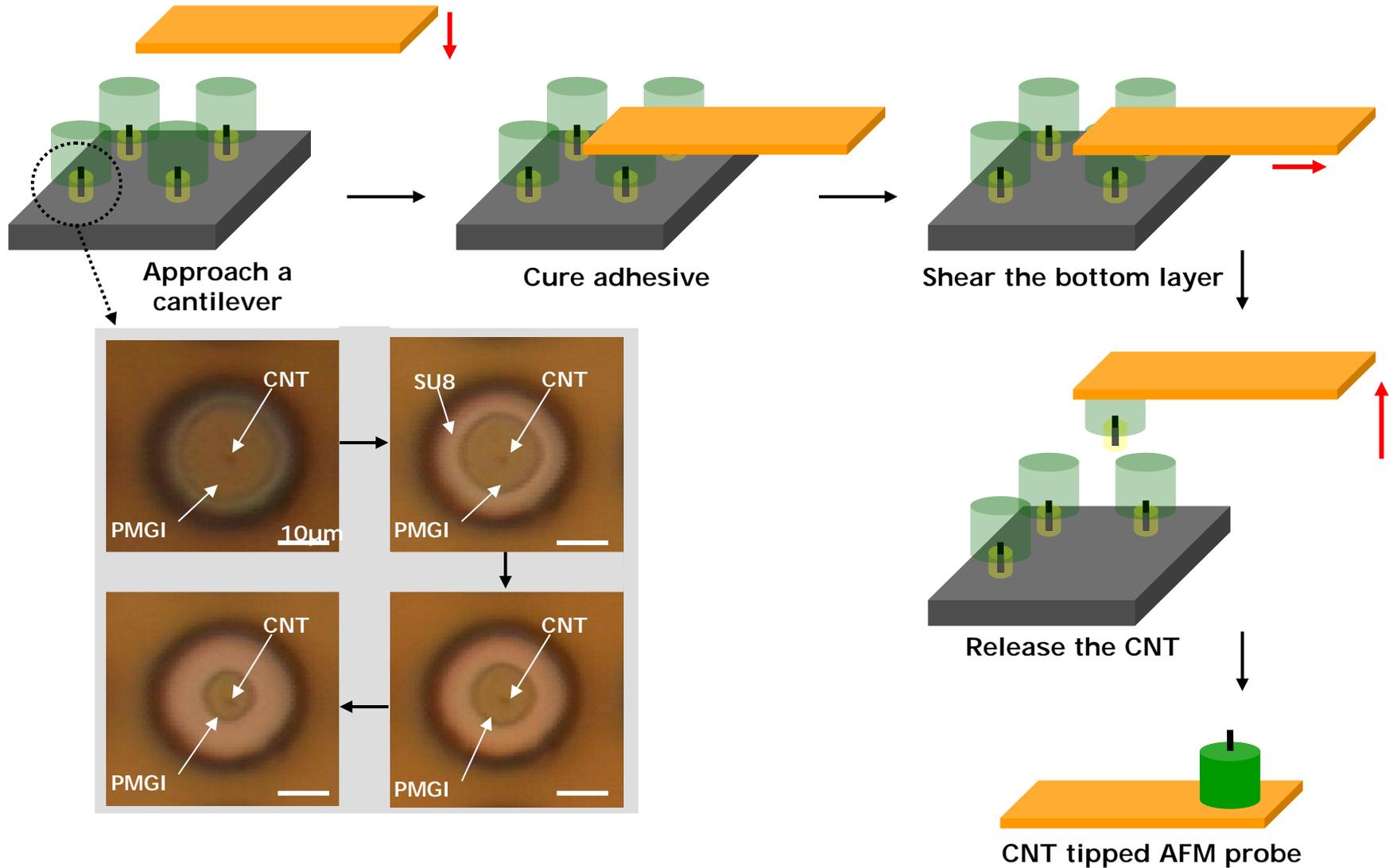
Guided Assembly

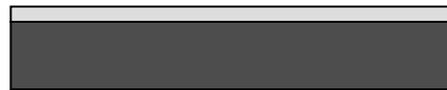
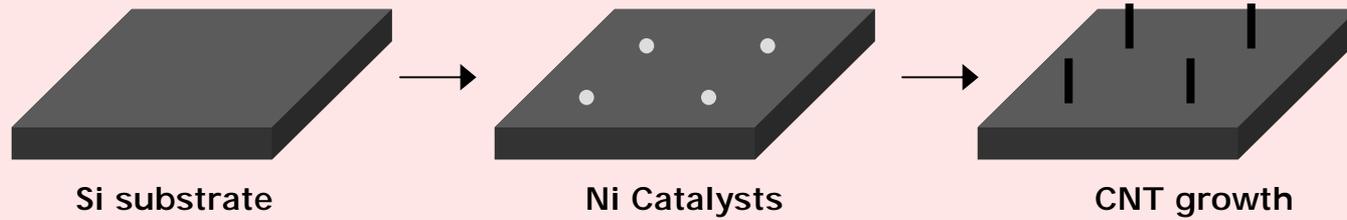


Fluidic Self-assembly

Alien Technology

# Directed Assembly of the Single Pellet





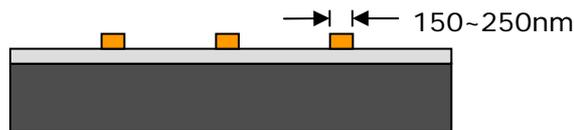
Ti (25nm) deposition



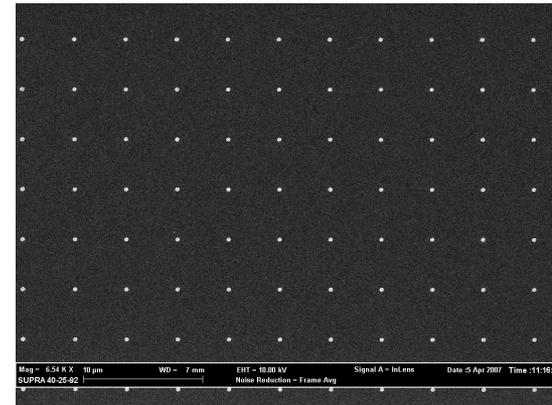
PMMA (100~125nm) coating



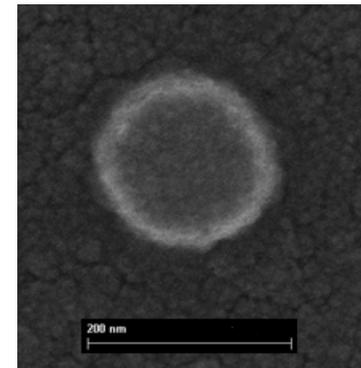
Electron-beam lithography



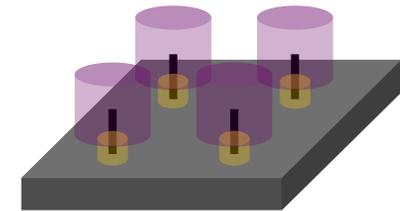
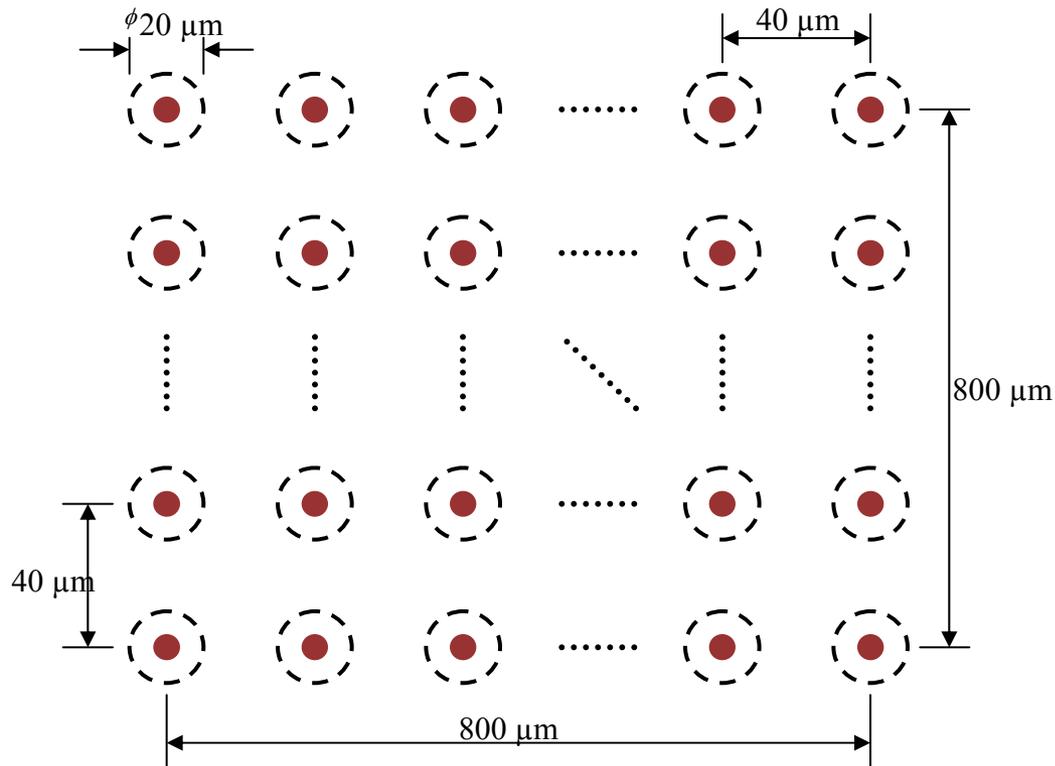
Ni (40 nm) deposition & liftoff



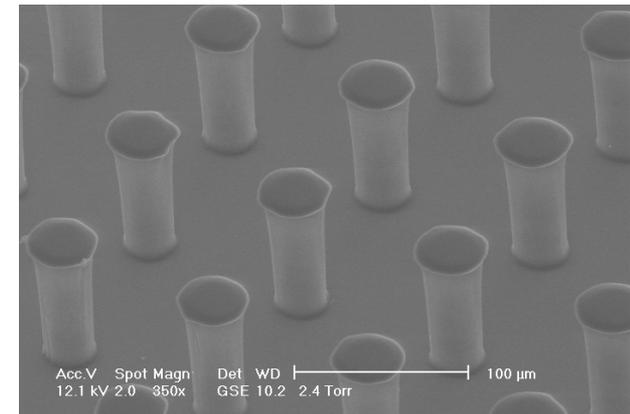
An array of Ni catalytic dots

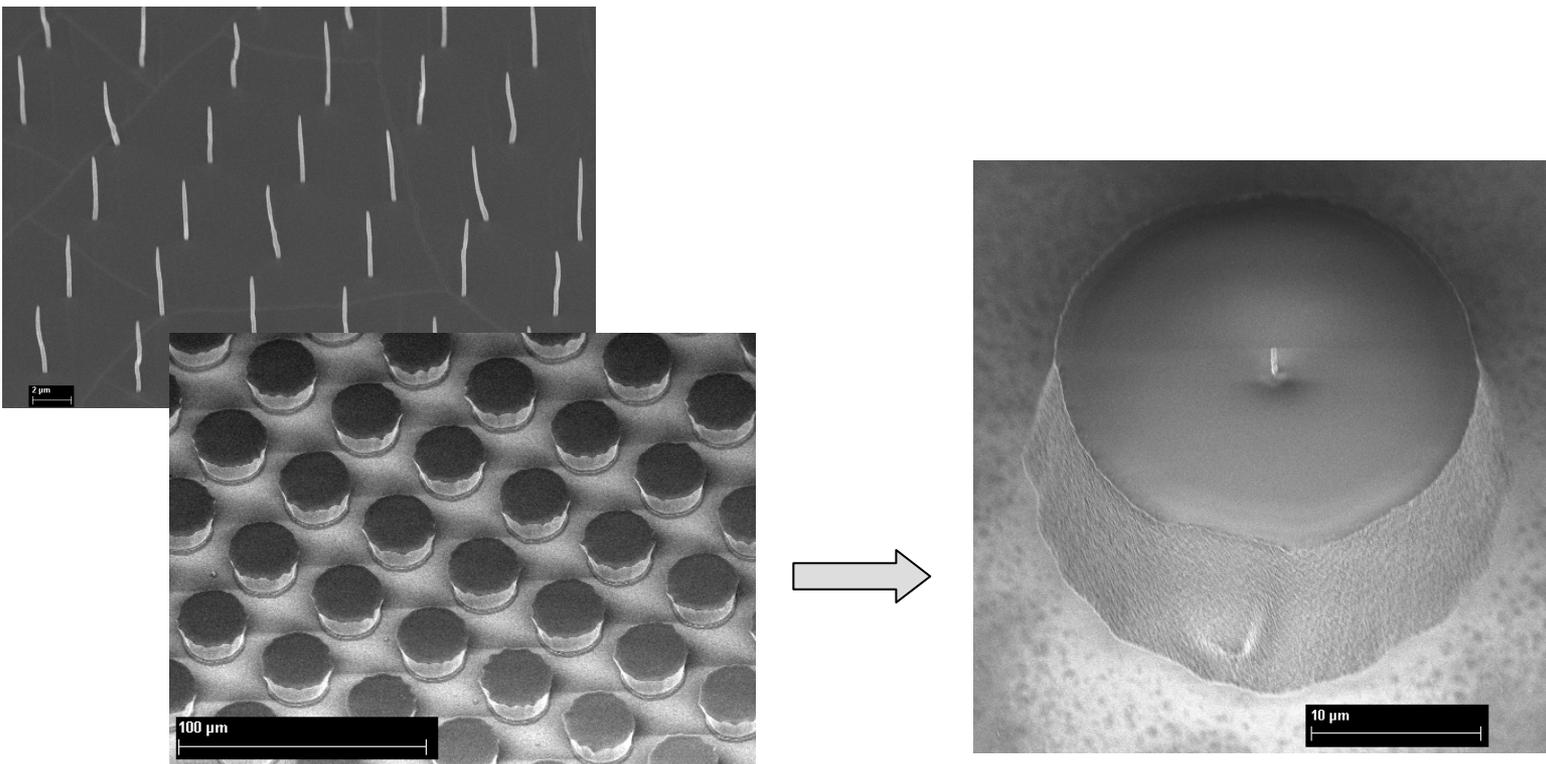


180nm in diameter



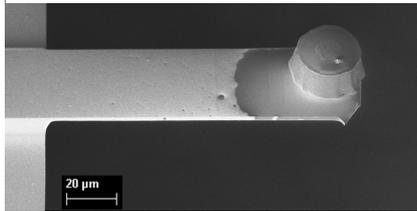
Encapsulation





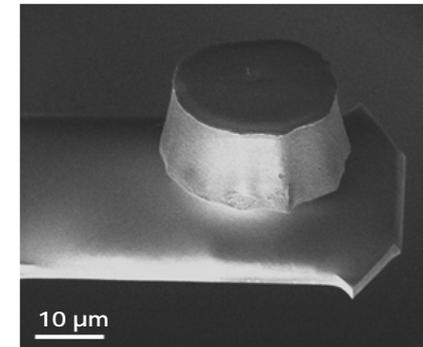
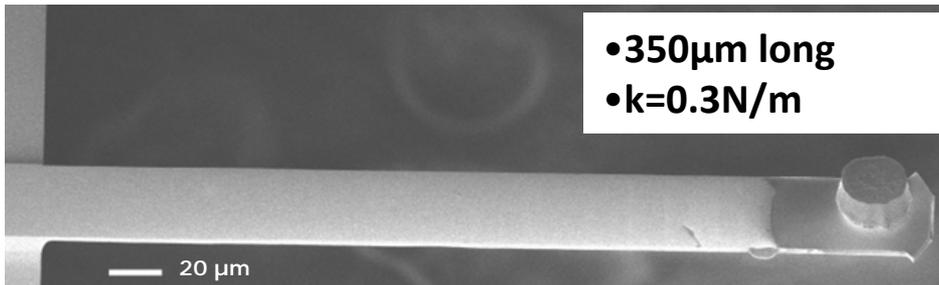
<b>Number</b>	one CNT
<b>Location</b>	The center of SU8 pellet
<b>Length</b>	1.5μm (the thickness of the bottom layer)
<b>Orientation</b>	The pellet axis

## Silicon cantilever (tapping mode)

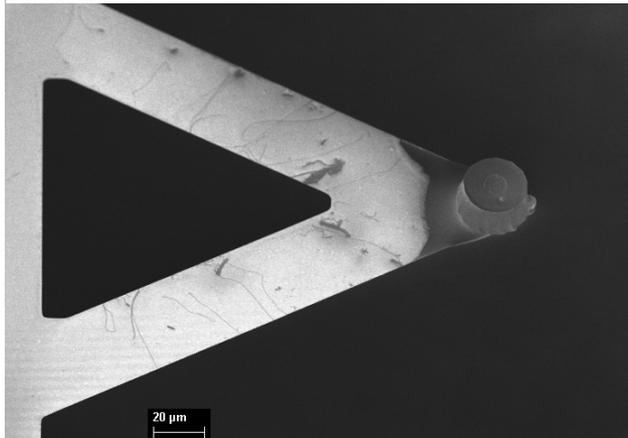


- 130 μm long
- $k=4.5\text{N/m}$
- $f=60\text{kHz}$

## Silicon cantilever (contact mode)



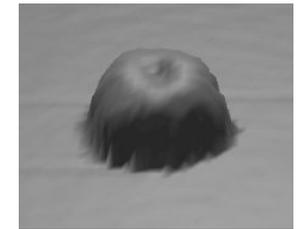
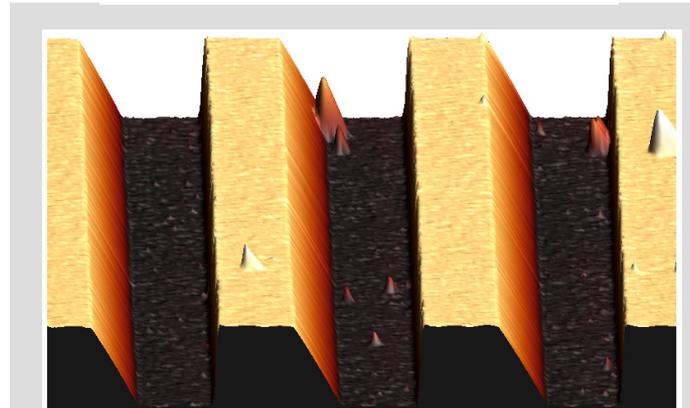
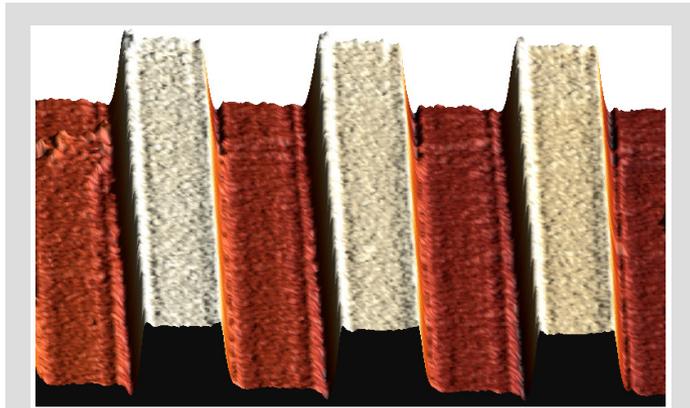
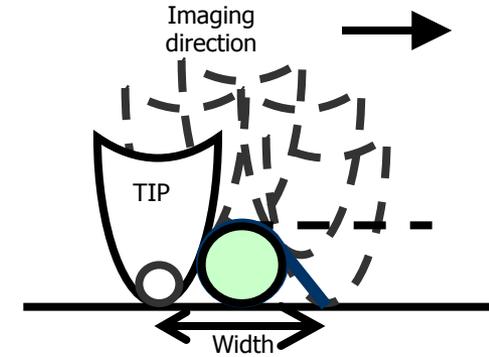
## $\text{Si}_3\text{N}_4$ cantilever (contact mode)



- 196 μm long
- $k=0.12\text{N/m}$
- Au/Cr coating

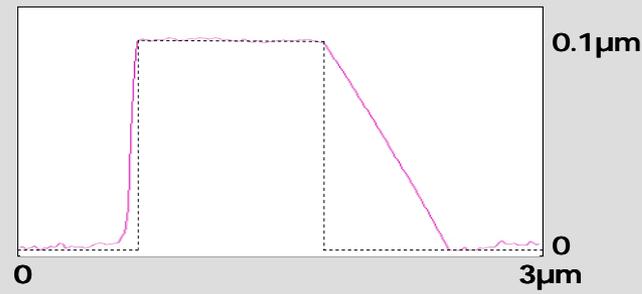
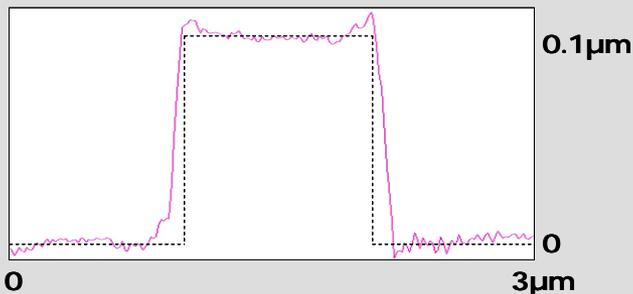
CNT probe  
(contact mode)

Pyramid Silicon probe  
(tapping mode)

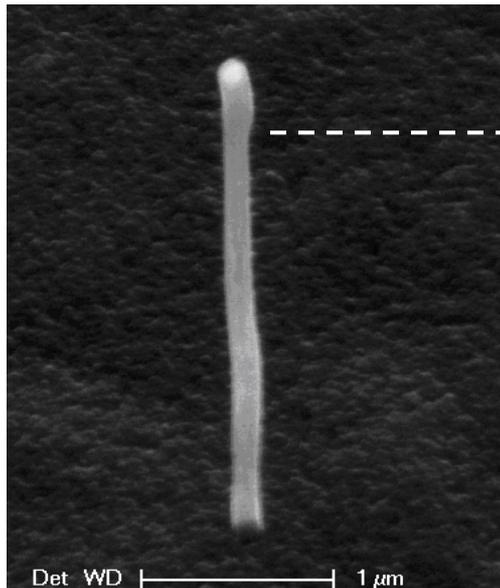


10 $\mu$ m

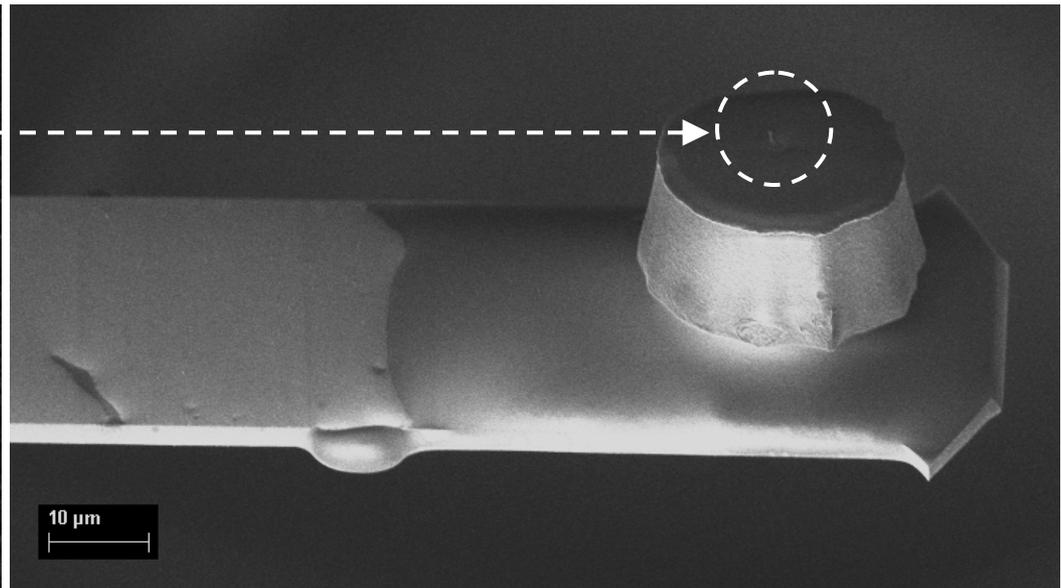
10 $\mu$ m



First demonstration of a deterministic assembly of individual nanostructures (carbon nanotubes) by transplanting assembly

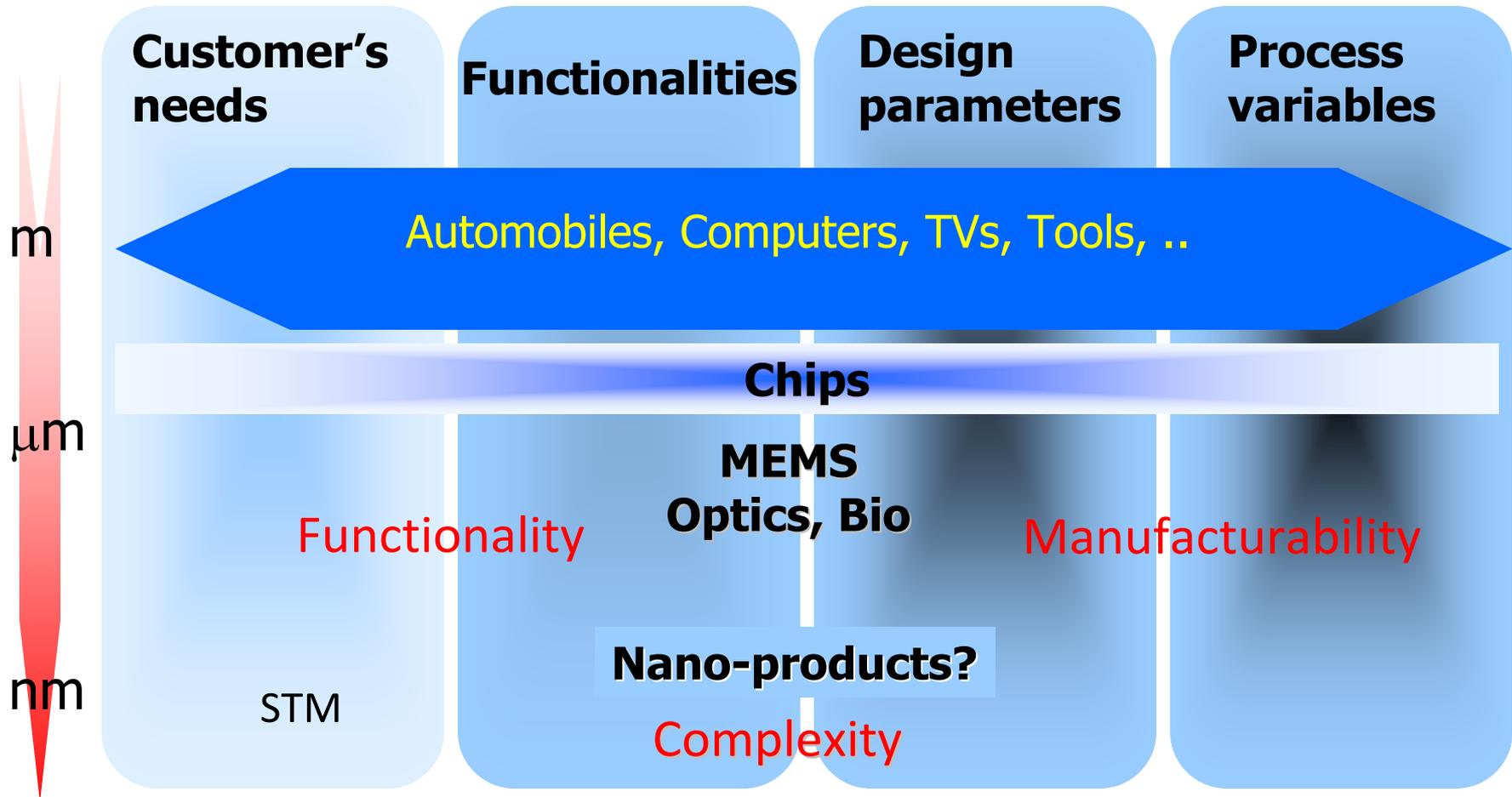


A single strand CNT



A CNT-tipped AFM probe

better process control and planning



# Computer modeling in nanomanufacturing-applications in cost and scale-up

**John Maguire PhD, DSc**

Air Force Research Laboratory  
Dayton, Ohio  
USA



# Self Assembly in Granular Materials

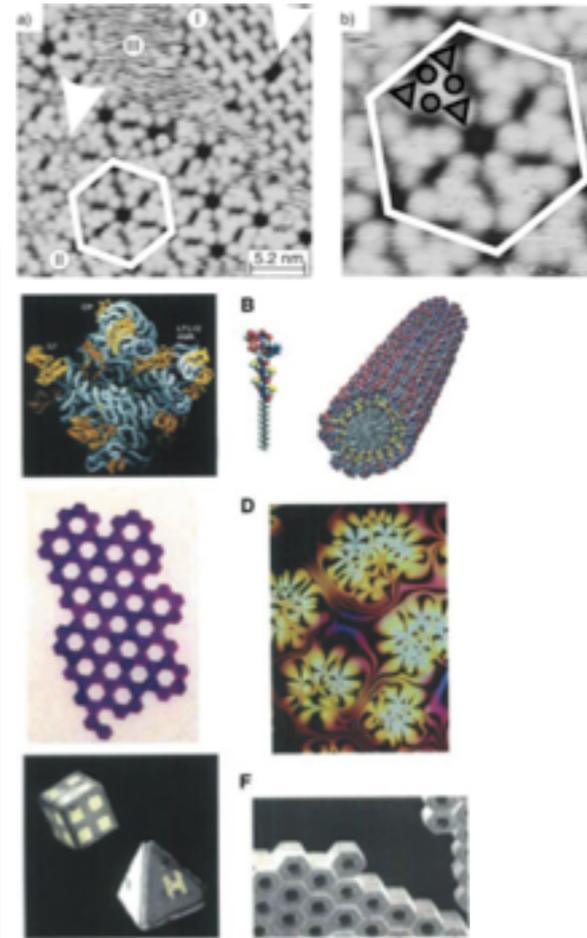
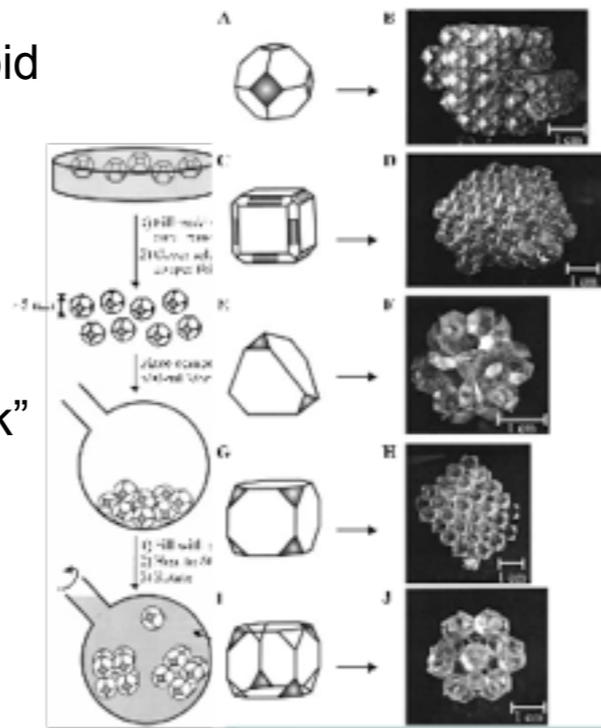
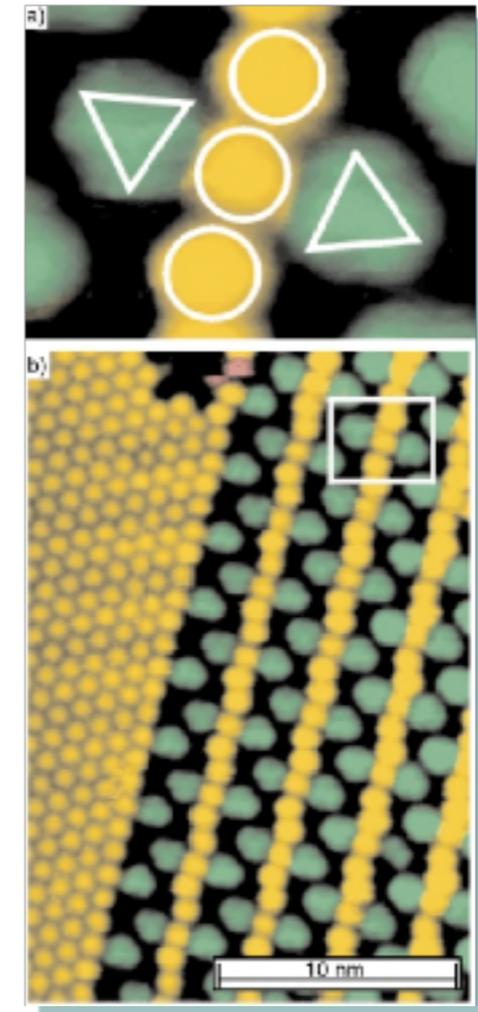
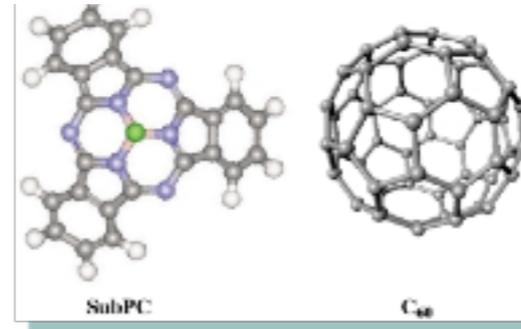
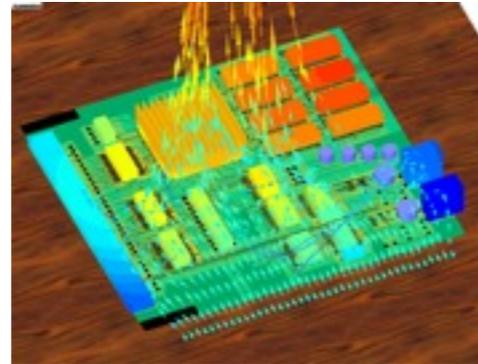
Spontaneous organization into complex patterns.

Particularly important as most granular materials are at some point “fluids”

Dissipative (Diffusion limited aggregation) vs. Static (protein folding / lipid bilayer formation) self-assembly.

What processes control self assembly? -> quite often dominated by “weak” interactions.

What is the FREE ENERGY in the mesoscopic regime?



G. Whiteside and B Grzyowski, Science **295** 2418 (2002)

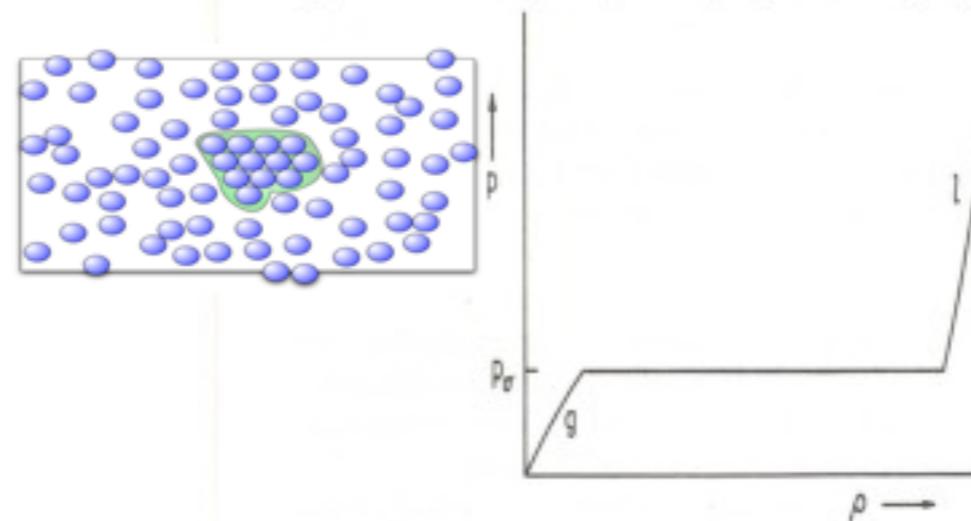
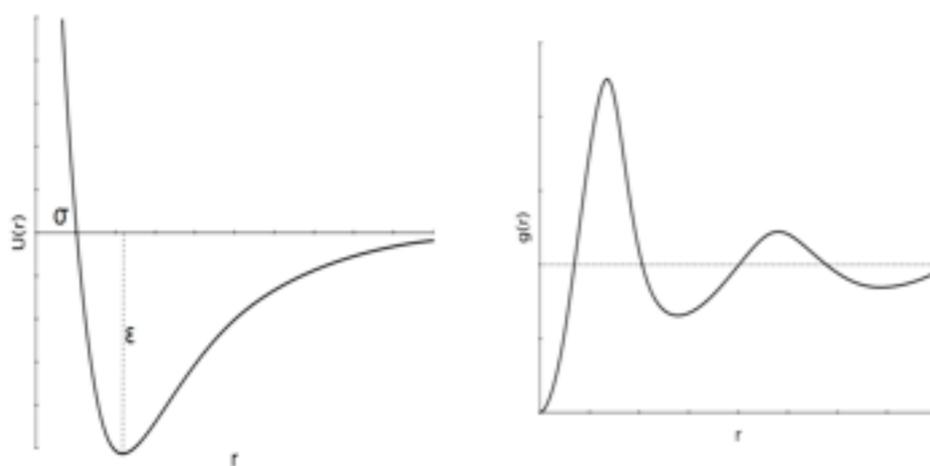
M. De Wilde et al. ChemPhysChem **10** 883 (2002)



# How big is "small"?

$$d\langle U \rangle = -PdV + TdS$$

$$P = -\left(\frac{d\langle U \rangle}{dV}\right)_S$$



## FARADAY LECTURE\*

### The Molecular Theory of Small Systems

By J. S. Rowlinson

PHYSICAL CHEMISTRY LABORATORY,  
SOUTH PARKS ROAD, OXFORD, OX1 3QZ

#### 1 Systems Large and Small

We are surrounded by (and indeed composed of) small systems—surfaces, bubbles, drops, colloids, emulsions, cells, membranes *etc.*—yet statistical mechanics, our principal theoretical tool for understanding the physical properties of matter at a molecular level is almost entirely the theory of the behaviour of infinitely large systems. Thus from any elementary text-book of thermodynamics we learn that the isotherm that connects the orthobaric states of a liquid and its vapour is a straight horizontal line of constant pressure, equal to the saturated vapour pressure (Figure 1). This result is strictly true, however, only in an infinitely large, and therefore, as

**Figure 1** The pressure as a function of density in a system at a fixed temperature. Only if the system is infinitely large is the central part of the isotherm,  $p_s$ , truly horizontal, and the junctions at its ends sharp

I shall argue, in an essentially uniform system. Clearly we need to extend our theoretical understanding if we are to explain at a molecular level the behaviour of the real finite world.

Progress towards this goal has been fitful. A key step was taken at the end of the nineteenth century by Rayleigh and van der Waals, but it is only recently that real progress has been made and the subject put on foundations which, although not entirely solid, are now sufficiently firm for many of our purposes.

\* Based on the Faraday Lecture, given at Imperial College, London, on 10th March 1983

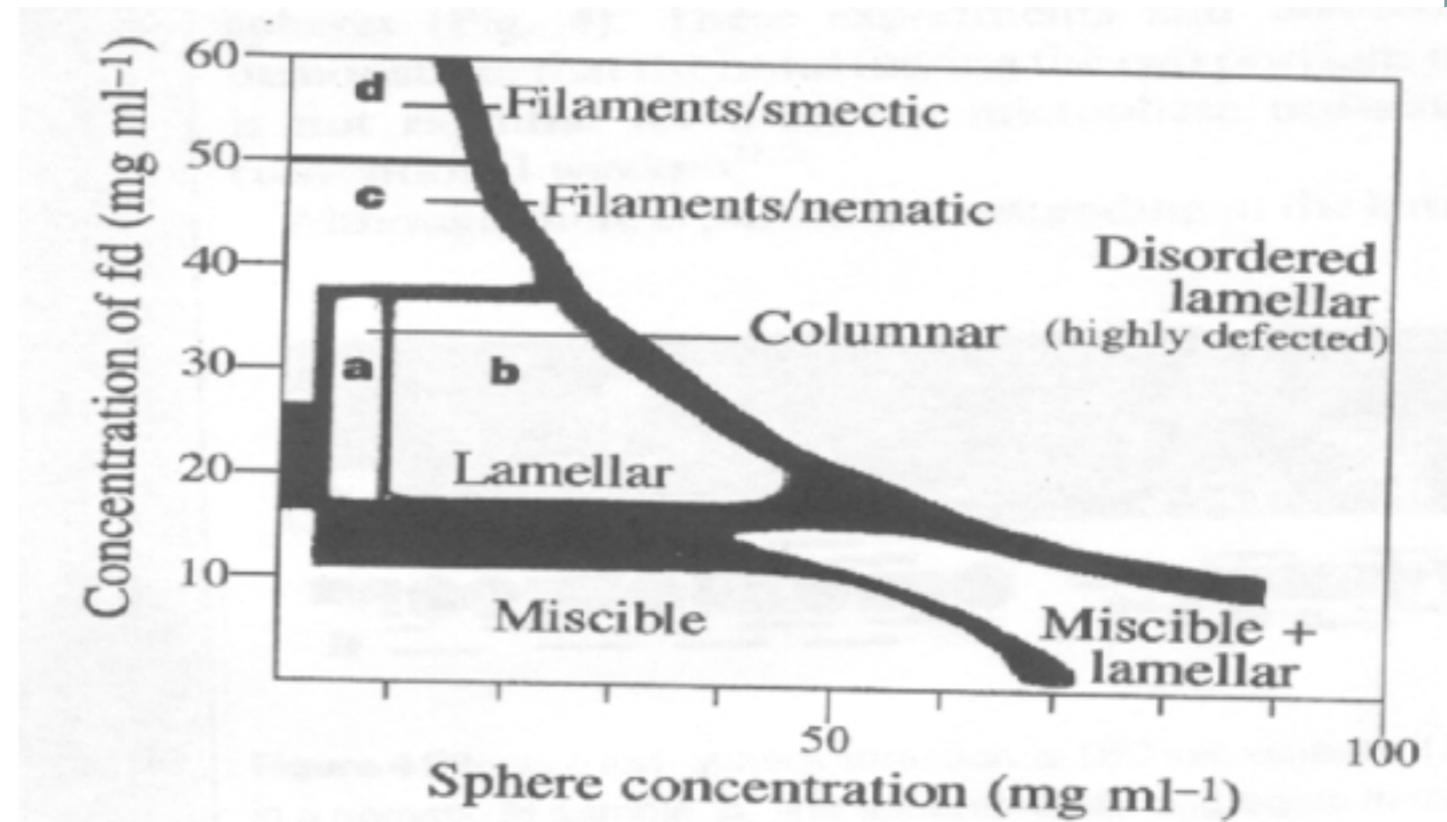
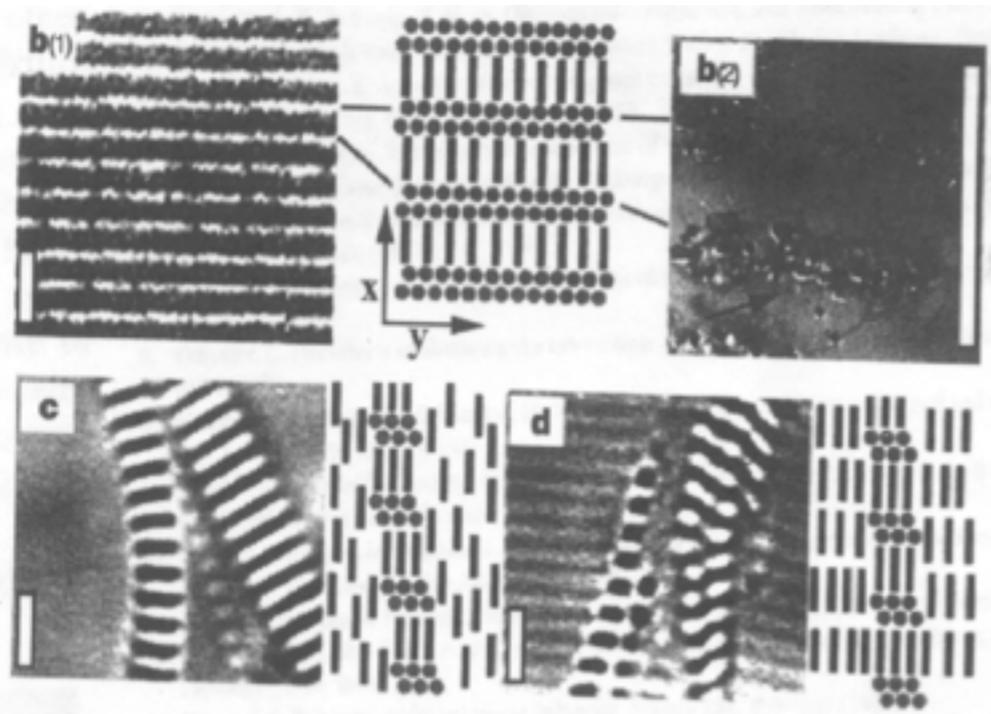
# Examples of common small systems

$$\langle U \rangle = \frac{\rho}{2} \int_0^{\infty} U(r) g(r) 4\pi r^2 dr$$

- **g** diverges near critical points---compressibility diverges/super diffusivity
- **U** becomes long range---gravitational potential (the universe is a nano system!)
- Upper limit ~system size ---within interfaces

**Correlation length~system size**

# The phase diagram in the nanoscopic regime can be used to Manufacture new structures of matter



Pathway to a whole range of new materials with Engineered Optical, mechanical, acoustic and thermal properties

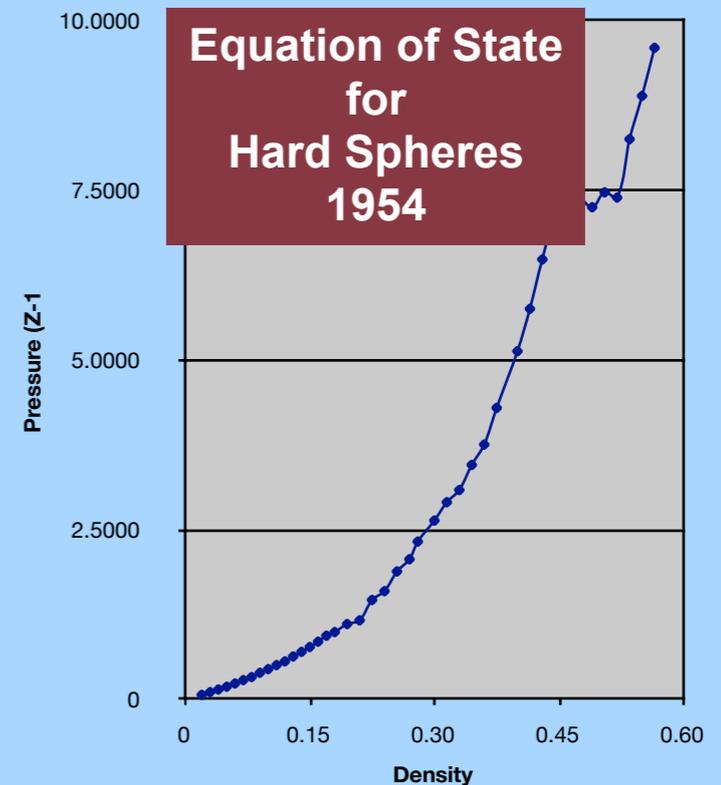
To PREDICT SUCH PHASE DIAGRAMS REQUIRES NEW METHODS THAT ARE "GRANULAR"

—diameter  $\sigma$  interact via potential energy function of the form :

$$u(r) = \infty \text{ for } r \leq \sigma, 0 \text{ for } r > \sigma$$

$$\left| (r_i + v_i t_c) - (r_j + v_j t_c) \right|$$

$$g(t) = \mathbf{u}_i(t) \times \mathbf{u}_j(t) \cdot \mathbf{r}_{ij}(t)$$



**HARD LINES**  
collision,  $g(t_c) = 0$ , solve for  $t_c$

D. Frenkel and J. Maguire, *Molecular Physics.*, 49(3), 503-541 (1983).

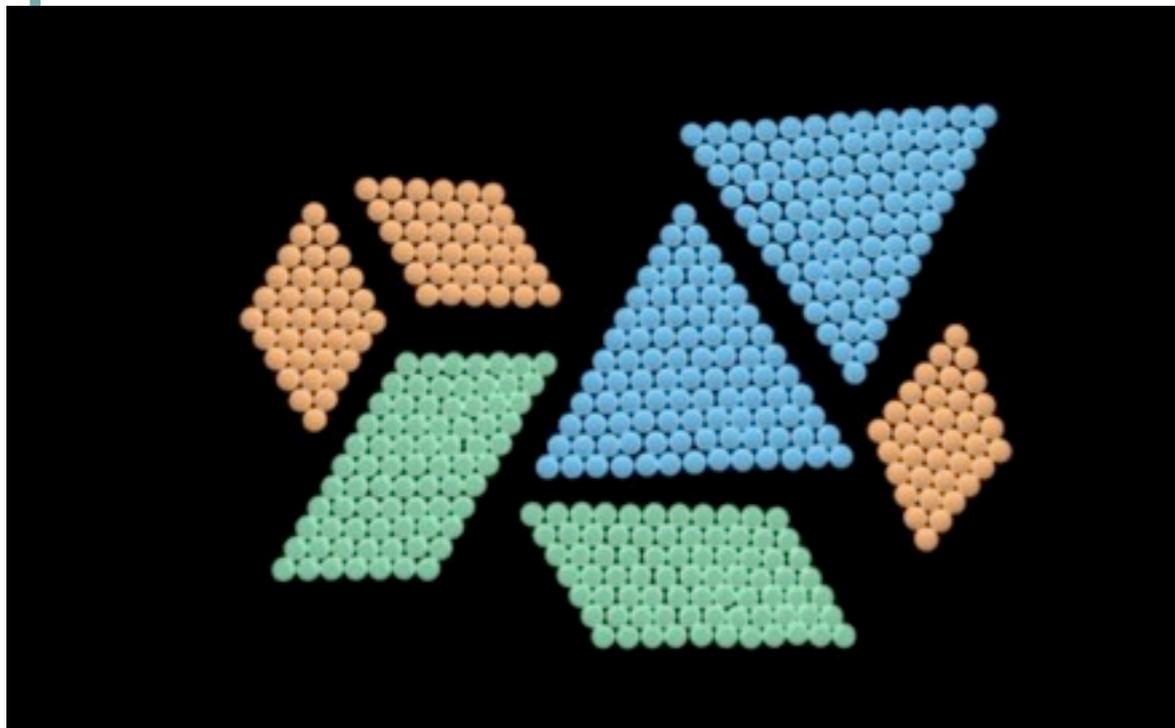
D. Frenkel and J. Maguire, *Phys. Rev. Letts.*, 47(15), 1025-1028 (1981)

J.F. Maguire, J.P. McTague and F. Rondalez, *Phys. Rev. Letts.*, 45(3),1891-1894, 1980.

# Single-body advantage



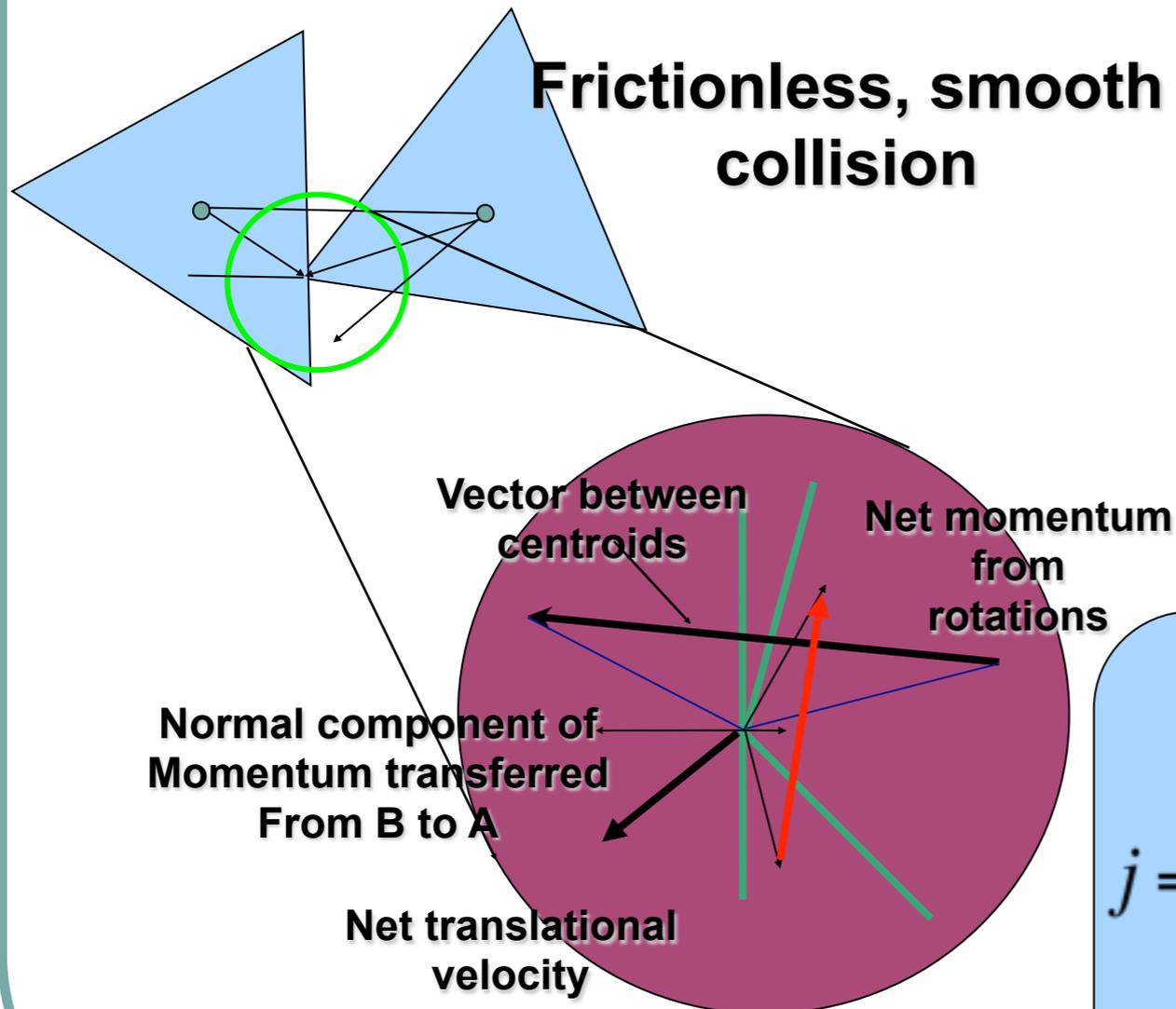
$$N^2 = 49$$



$$N^2 = 444^2 = 197136$$

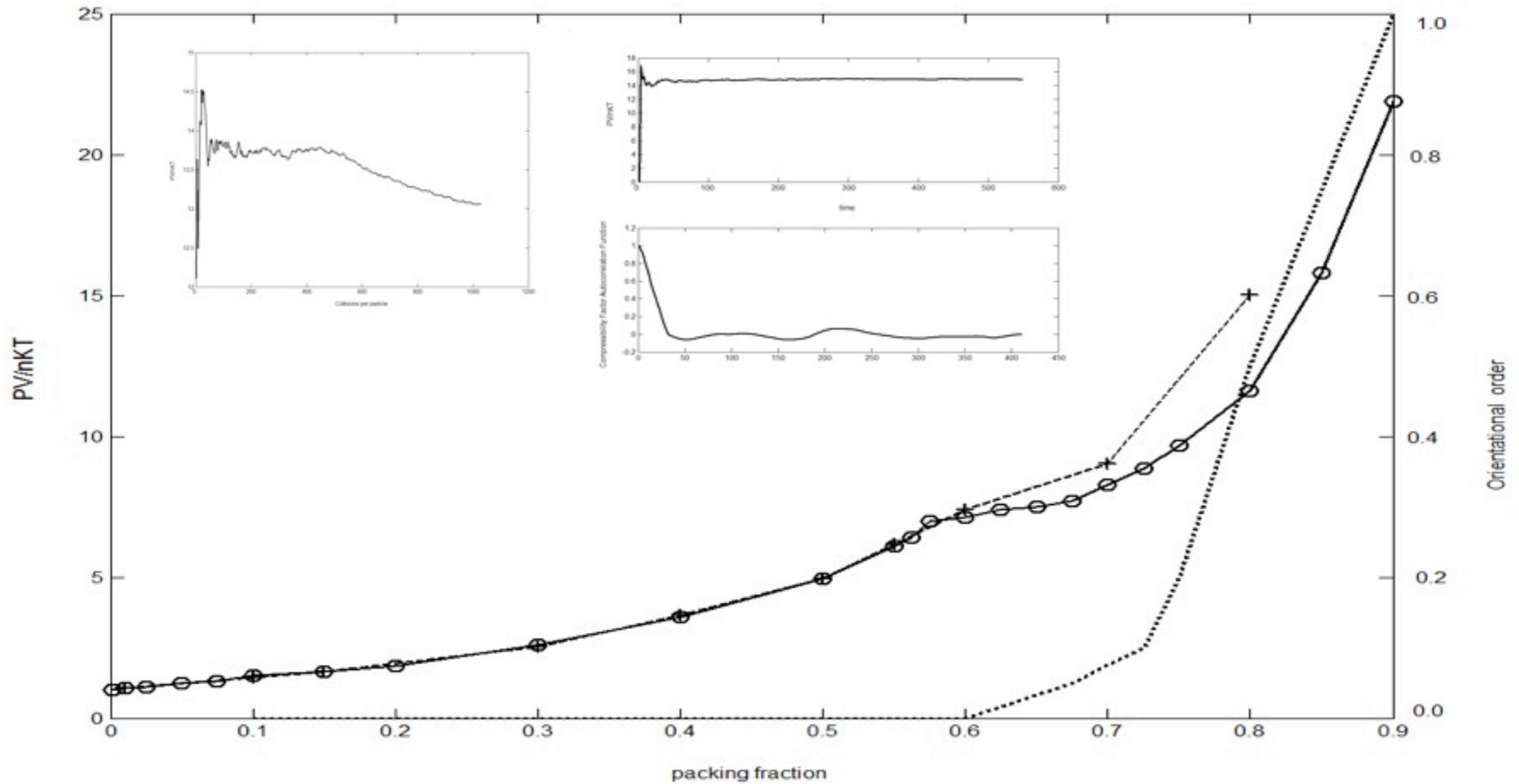
# Dynamics for Hard Triangles

## Frictionless, smooth collision



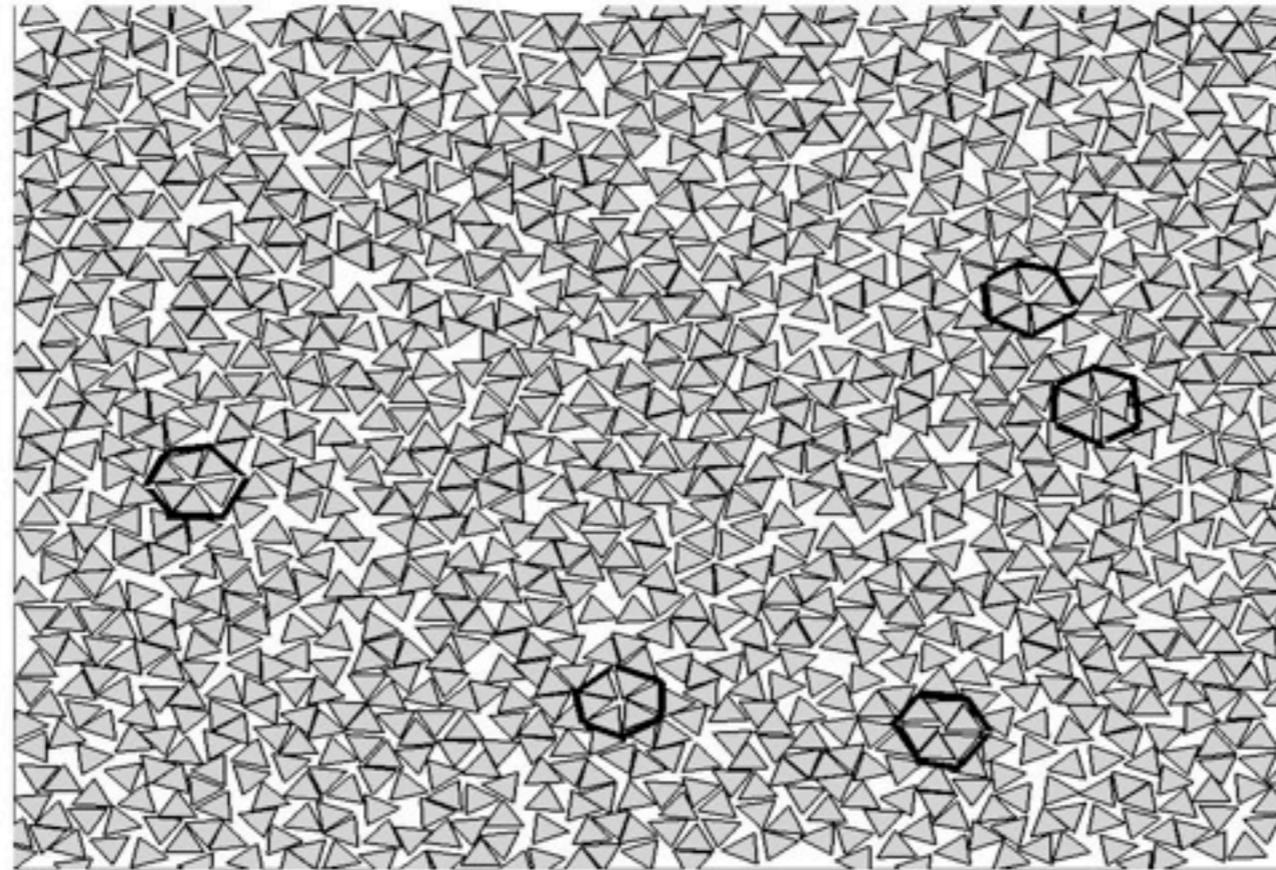
- Conservation of momentum and energy are the key factors to consider.
- The impulse transferred between the objects can be shown to be .

$$j = \frac{-(1+e)v_1^{AB} \times n}{n \times n \left( \frac{1}{M^A} + \frac{1}{M^B} \right) + \frac{(r_{perp}^{AP} \times n)^2}{I^A} + \frac{(r_{perp}^{BP} \times n)^2}{I^B}}$$



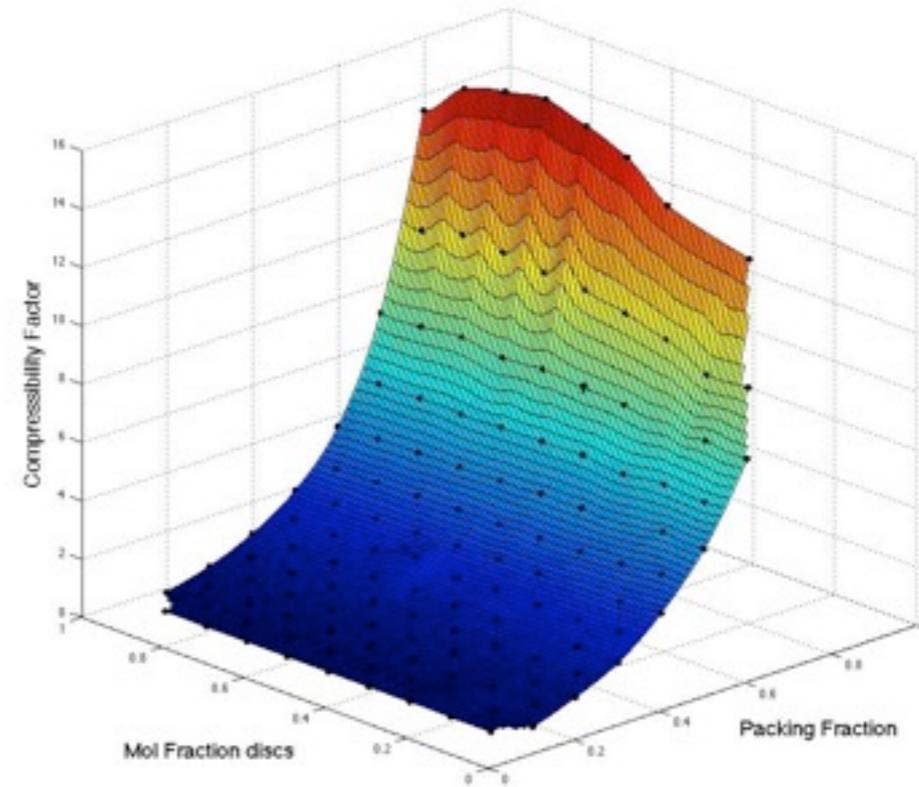
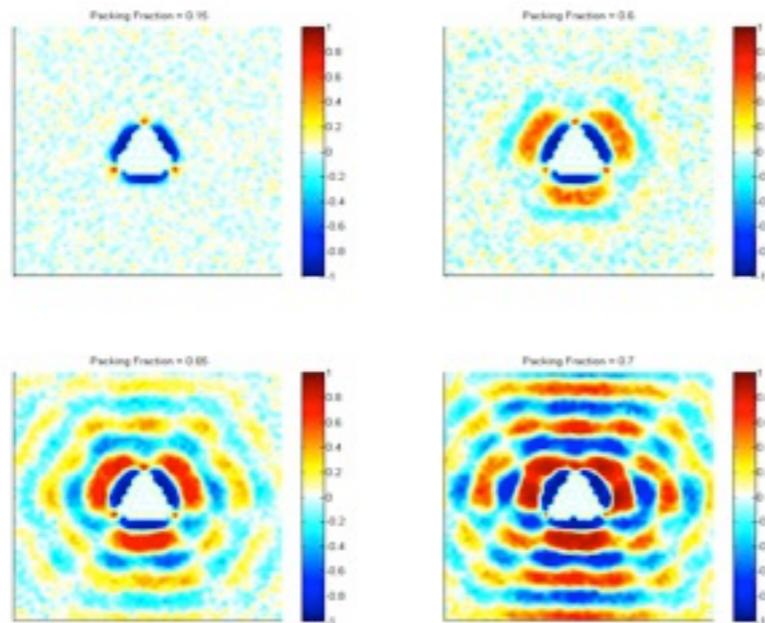
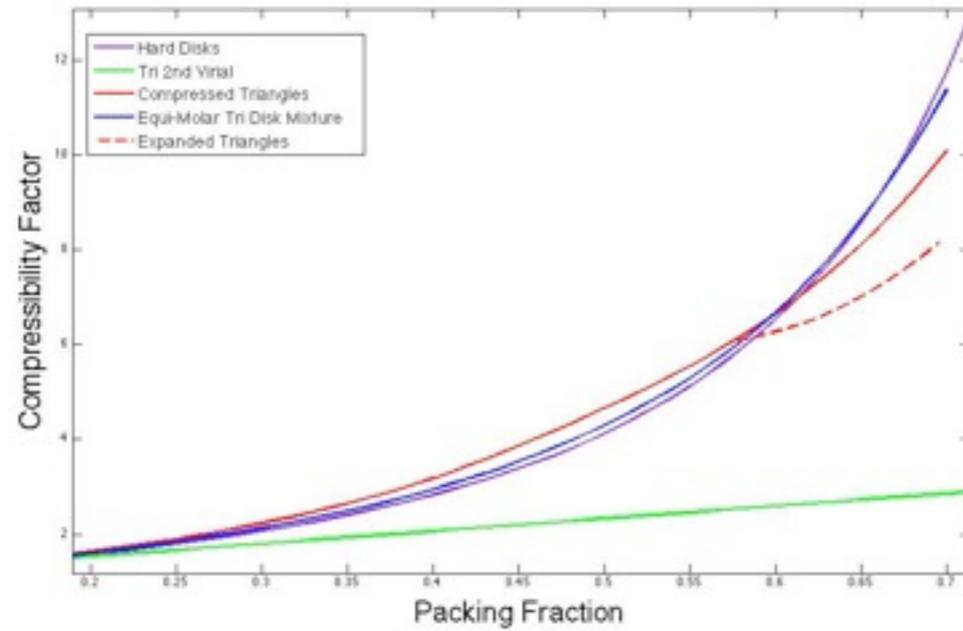
- Equation of state for hard triangles in two dimensions. The open circles connected by the solid line correspond to runs in a expansion cycle, while the crosses connected by the dashed line correspond to runs in a compression cycle. The dotted line shows the hexagonal orientational order factor  $g_6$  as a function of packing fraction. The insets show the relaxation time required for equilibration following expansion (top right) and compression, top left

First observation of the “hexatic” phase  
Note the appearance of a quasi-crystal structure



- Figure 10. Configuration in the neighborhood of the transition highlighting the tendency to form long-lived hexagonal clusters. Note also the visual similarity to quasicrystal.

# Investigating Composition Dependence



## Summary

- Modeling thermodynamics and kinetics of self assembly will be essential in scale-up of nanomanufacturing.
- Cost/quality/scale-up depends on long-range structural coherence.
- New codes/approaches will be needed to bridge distance-time-scale challenges.



# Researchers Carve with Electricity at the Nanometer Scale

**Students:** V. Kalyanasundaram,<sup>1</sup> Kumar R. Virwani<sup>2</sup>  
**Investigators:** Ajay P. Malshe,<sup>1</sup> K.P. Rajurkar<sup>3</sup>  
**Collaborator:** E.J. Taylor<sup>4</sup>

<sup>1</sup> University of Arkansas  
<sup>2</sup> IBM Almaden  
<sup>3</sup> University of Nebraska  
<sup>4</sup> Faraday Technologies

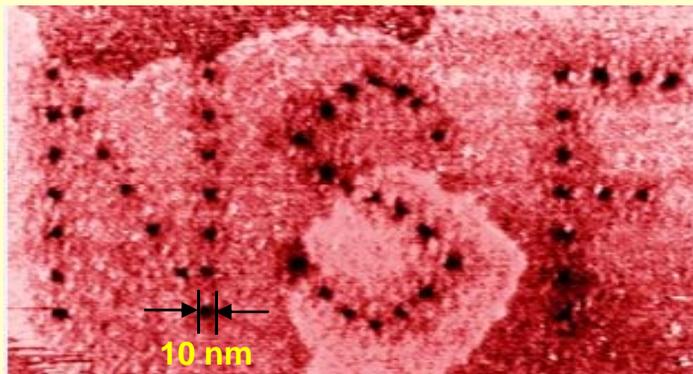
## GOALI-CMMI Grant # 0423698

**Issue:** One of the grand challenges of nanomanufacturing is to nano-machine a diverse set of materials, for example, from gold metallized polymers for electronic applications to difficult-to-cut titanium alloys for bio-medical applications, at low cost and high speed.

**Objective:** To develop a process namely nano Electro Machining (nano-EM) called Electric Pen Lithography (EPL), which can generate precise nano features and structures in hard and difficult-to-cut materials in a less controlled environment, at low cost and perform *in situ* metrology.

**Approach:** In a breakthrough, by applying electric current through a thin film of oil molecules, engineers have developed a new method to precisely carve arrays of tiny holes only 10 nanometers wide into sheets of gold (see *Figure*).

**Accomplishments:** (1) Fabricated nano-tools of tip radius 35 nm ( $\pm$  10 nm) and developed *in situ* characterization methods, (2) Performed electrical discharge characteristics analysis in Direct Current (DC) and pulsed bias modes, (3) Analyzed the repeatability performance of this nanomanufacturing process (4) Modeling of the nano-EM machining interface to understand the dielectric molecular medium organization under electro-mechanical boundary conditions, (5) Wear characteristics of nano-tools after nano-EM machining using TEM (6) one patent pending, 6 papers published and 1 under review.



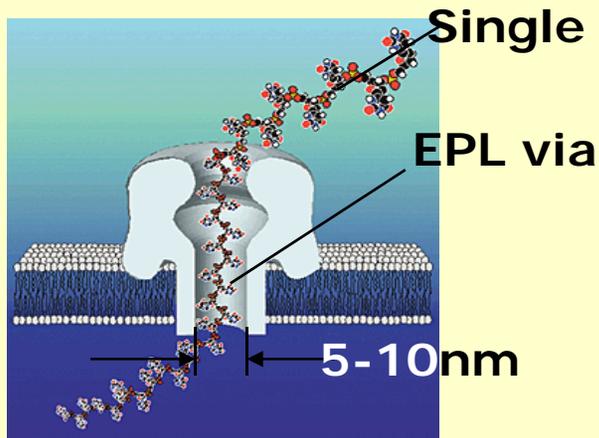
← The holes that spell "NSF" are only 10 nanometers in diameter on gold surface. Please visit the following URL for more details:  
[http://www.nsf.gov/news/news\\_summ.jsp?cntn\\_id=104304&org=NSF](http://www.nsf.gov/news/news_summ.jsp?cntn_id=104304&org=NSF)

# Drivers and objectives for nanoEM, named Electric Pen Lithography (EPL)

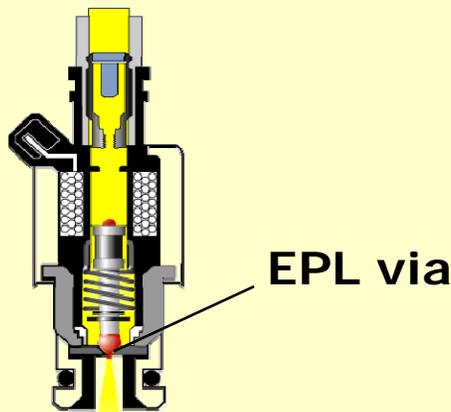
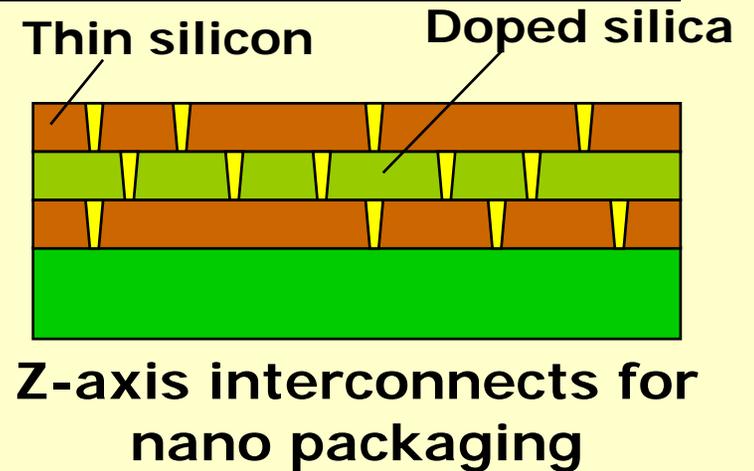
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- Nanomanufacturing of features in difficult-to-machine materials using electric fields under ambient conditions at low cost and high speed
- Development of a process analogous to macro and micro scale electric discharge machining on nanoscale using a Scanning Probe Microscopy platform
- Instrumentation advances to define nanometer scale gaps, apply user-defined pulses and monitor current events for process monitoring and optimization
- Exploring the science about the generation and relaxation mechanisms associated with nano-strain
- Development of methods to quantify the quality of nanoscale tools *in situ* instrumentation
- Understanding machining mechanisms in field based nanomanufacturing with regards to nanoscale confinement and interfacial behavior
- Understanding the behavior of dielectric molecules & chains under intense electric fields

# Potential EPL Applications

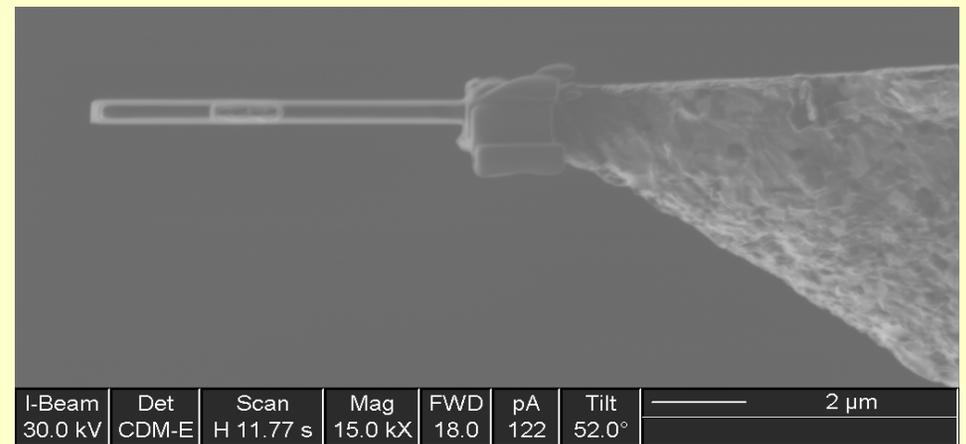


Single DNA detection devices



Nanojets for fuel injectors<sup>1</sup>

<sup>1</sup>[www.howstuffworks.com](http://www.howstuffworks.com)

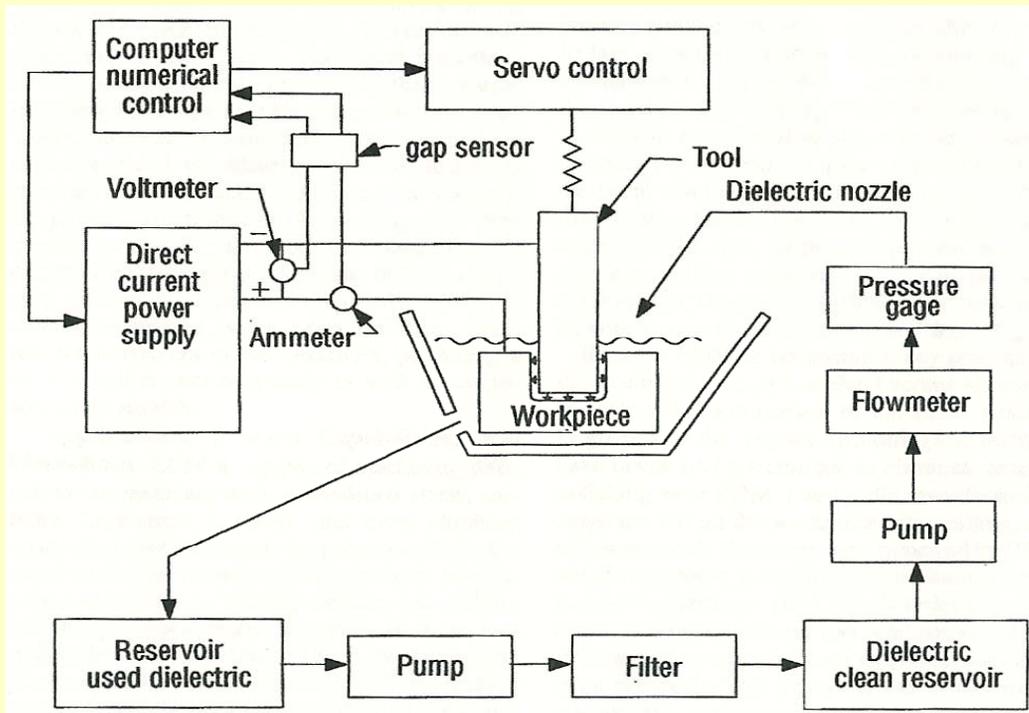


*in situ* TEM sample preparation

# Macro, micro EDM and nano-EM

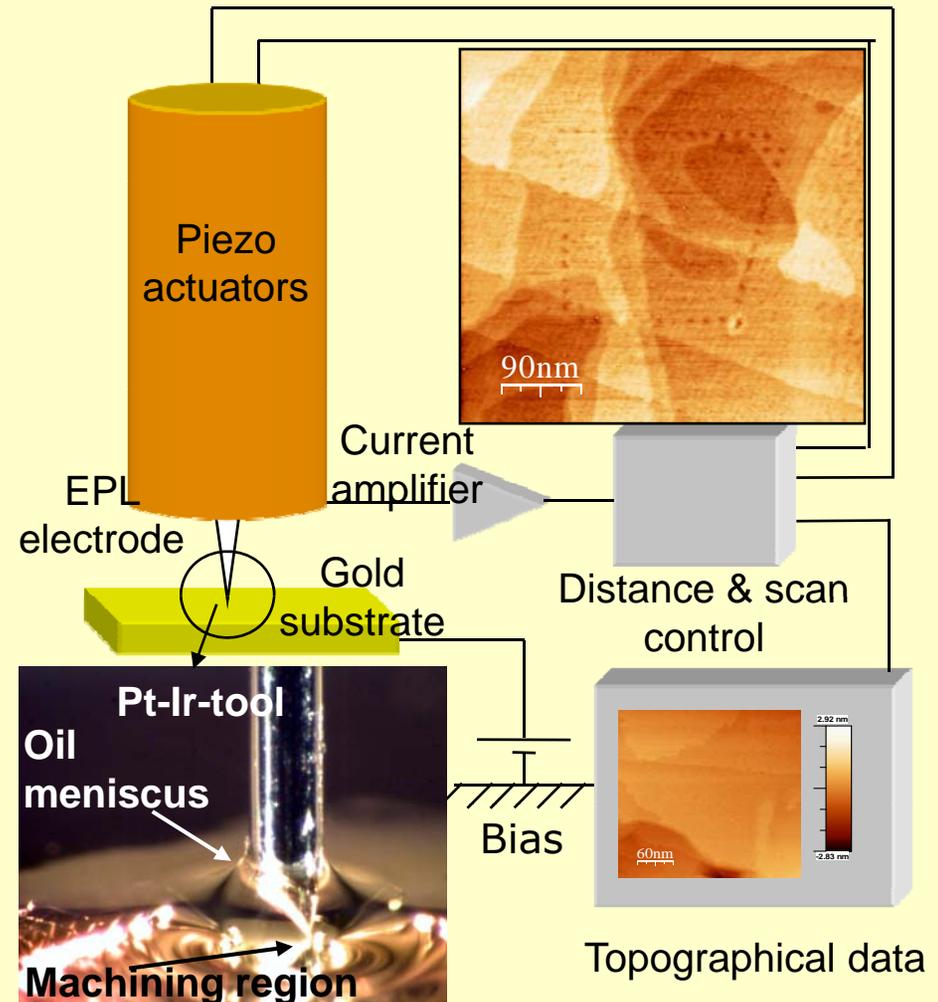
	Macro EDM	Micro EDM	Nano-EM
Electrode material	Copper, Tungsten, Graphite	Tungsten, Copper	Etched Tungsten and Platinum-Iridium alloys
Dielectric (strength)	EDM Oil (~30kV/2.5mm)	DI water (80) & EDM oil (~30kV/2.5mm)	n-decane & EDM Oil (>55kV/2.5mm)
Operating Voltage	40-400V (pulsed)	40-200V (pulsed)	2.5-30V (DC and Pulsed)
Breakdown field strength	$10^7 - 10^8$ V/m	$10^7 - 10^8$ V/m	$10^9$ V/m
Electrode diameter	~ few mms	~5 $\mu$ m (reported)	15-30nm
Breakdown gap	0.0127-0.0508mm	1-10 $\mu$ m	0.5-30 nm
Material removed per breakdown	62700 $\mu$ m <sup>3</sup>	5000 $\mu$ m <sup>3</sup>	1350nm <sup>3</sup> (?)
Tool wear per breakdown	20000 $\mu$ m <sup>3</sup>		11065nm <sup>3</sup>
Dielectric recovery time	1ms		1ms
Pulse duration	0.1-8ms		0.1-2ms
Total cycle time	20ms		3ms

# Experimental set-up for EPL



## Schematic of electrical discharge machining (EDM) set-up<sup>1</sup>

1 "Handbook of design manufacturing and automation", R. C. Dorf, A. Kusiak

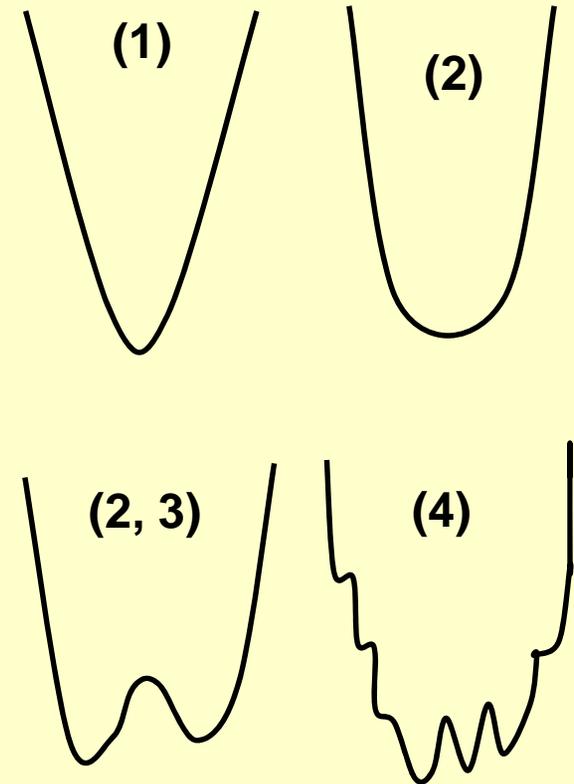
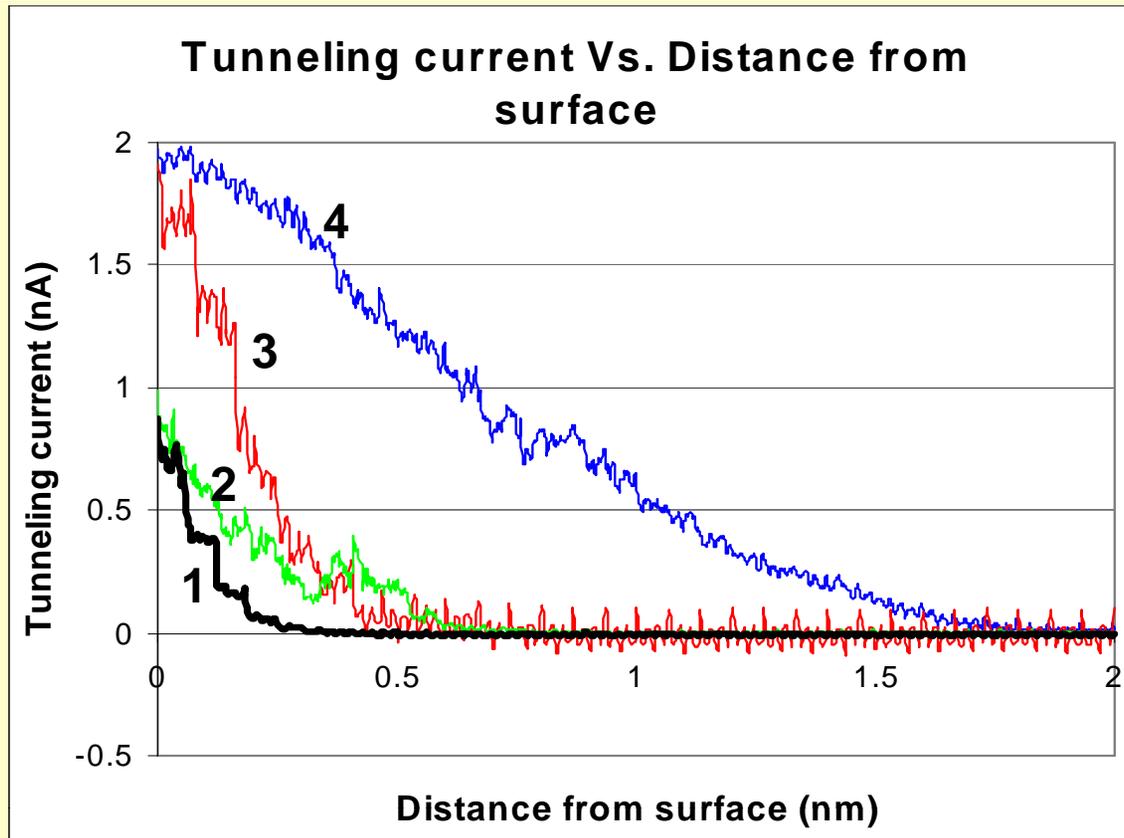


# EPL process - Advantages

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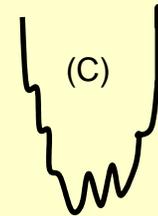
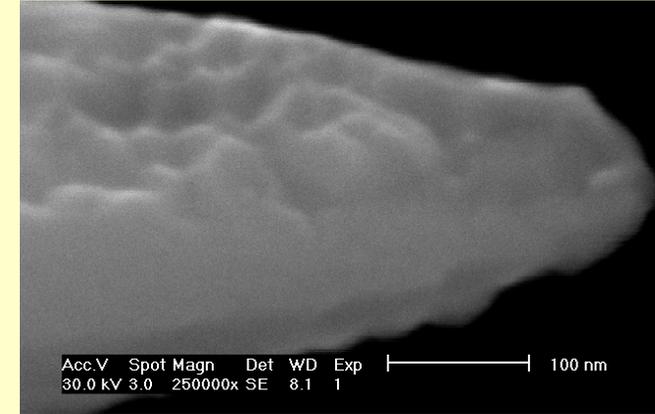
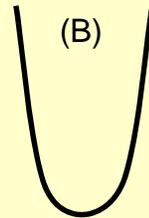
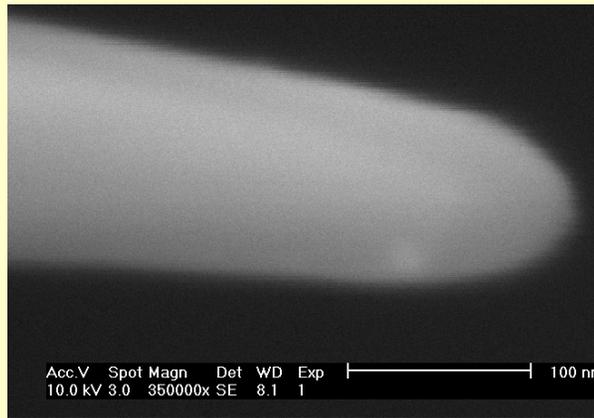
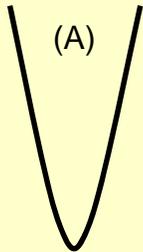
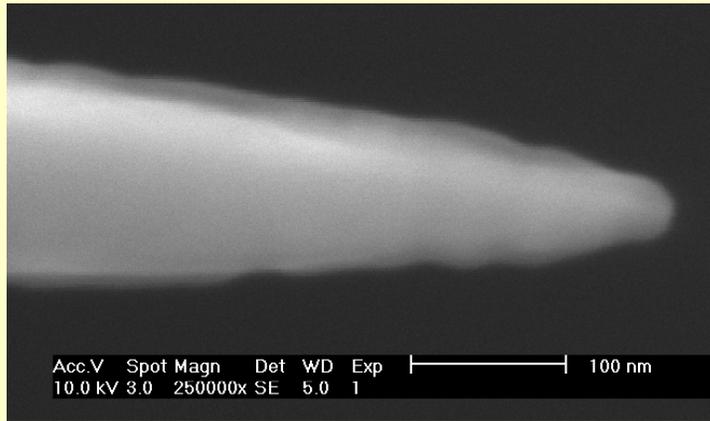
- ✍ Non-contact processing
- ✍ *in-situ* metrology of features
- ✍ In-line nano tool quality evaluation
- ✍ Use of small quantity of operator and environment friendly dielectrics
- ✍ Performed at room temperature and pressure
- ✍ Can be performed on conducting and semi-conducting materials
- ✍ Material removed can be easily flushed away
- ✍ Material removal rate can be controlled to a monolayer at a time
- ✍ Low cost

# Nano-tool analysis using current displacement (I-Z) curves



- Electrochemical etching methods were used to manufacture nano tools and the tool quality was quantified using current vs. displacement spectroscopy curves *in situ* EPL set-up
- Tools for which the tunneling current dropped to zero at less than or equal to 4Å away from the workpiece machined consistent features.

# Illustration of STM tips



❖ Tunneling current drops to zero at  $\leq 4\text{\AA}$

❖ Gives atomic resolution topographic scans

❖ Provides consistent nanoEM machining and hence are always used

❖ Tunneling current drops to zero at  $\geq 4\text{\AA}$  and  $\leq 8\text{\AA}$

❖ Gives surface features distinguishable topographic scans

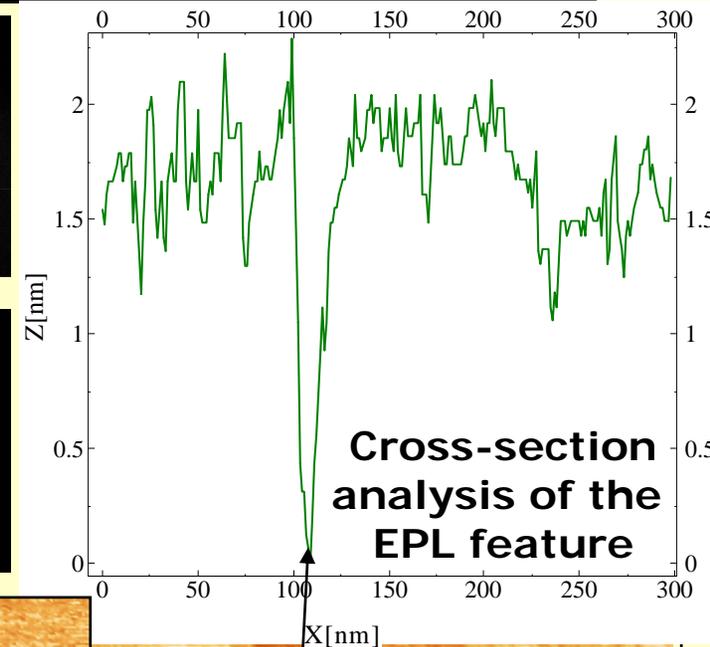
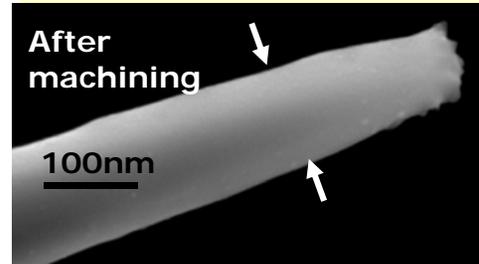
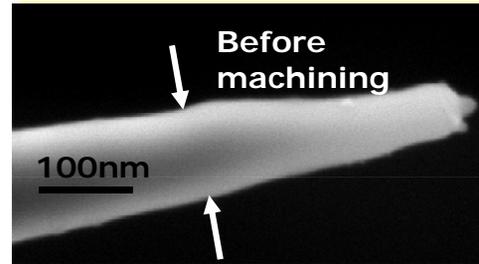
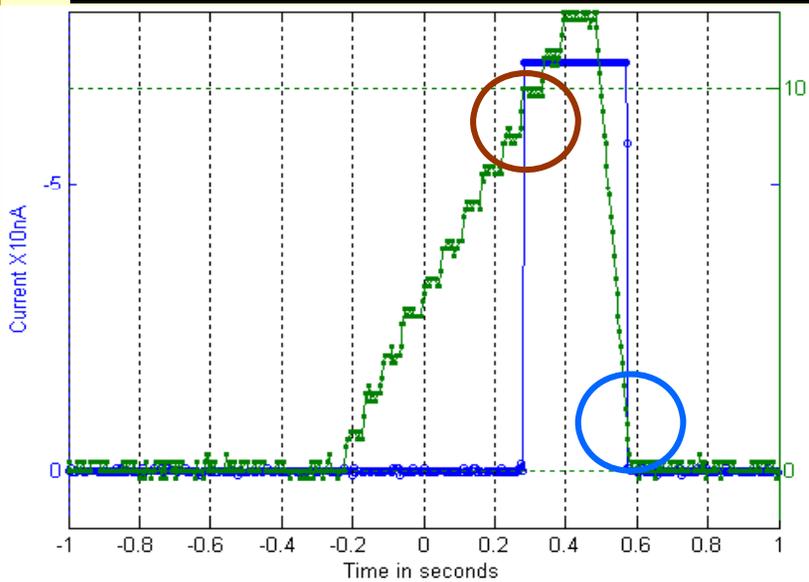
❖ Provides non-consistent nanoEM machining

❖ Tunneling current drops to zero at  $\geq 8\text{\AA}$

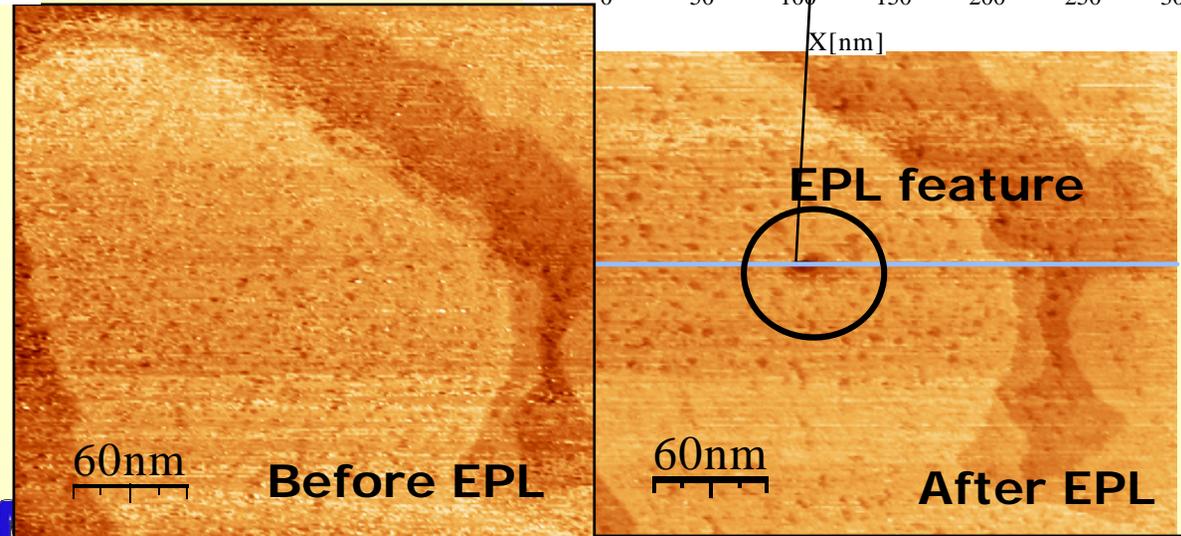
❖ Gives less-resolution topographic scans

❖ Not suitable for consistent nanoEM machining

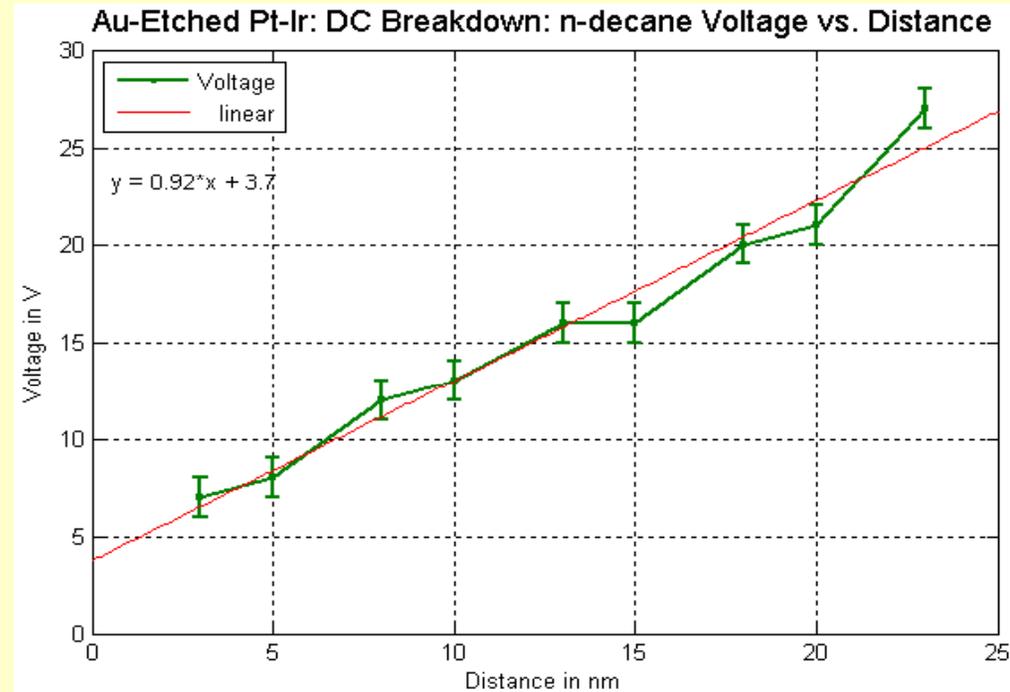
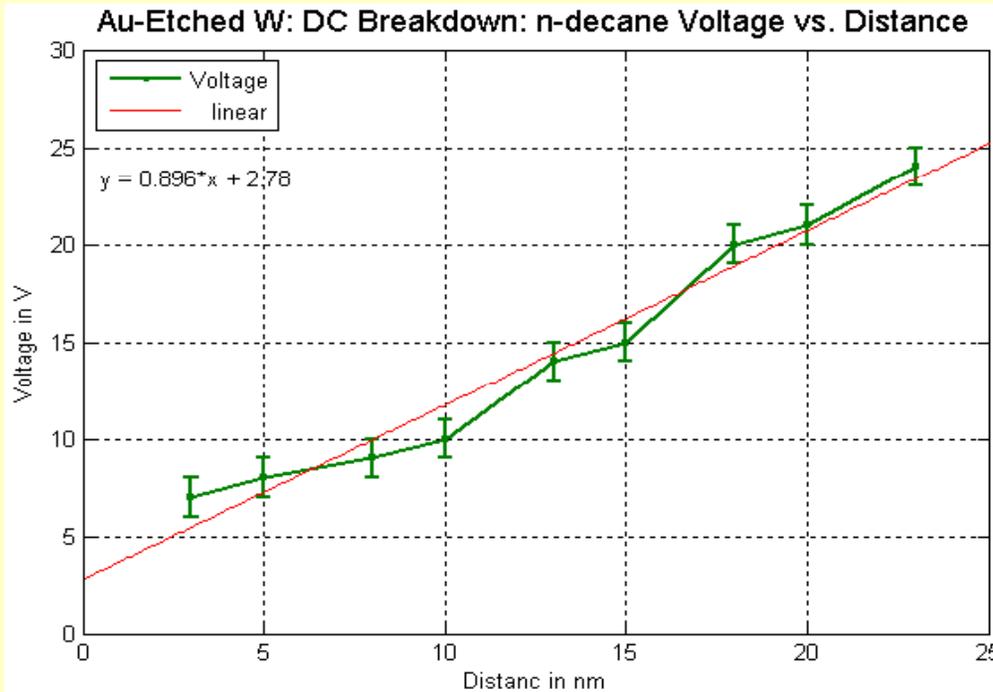
# DC breakdown machining



**Tool:** Etched Tungsten  
**Workpiece:** Hydrogen flame annealed atomically flat gold  
**Dielectric:** n-decane  
**Gap:** 10nm  
**Tool polarity:** Negative  
**Workpiece polarity:** Positive

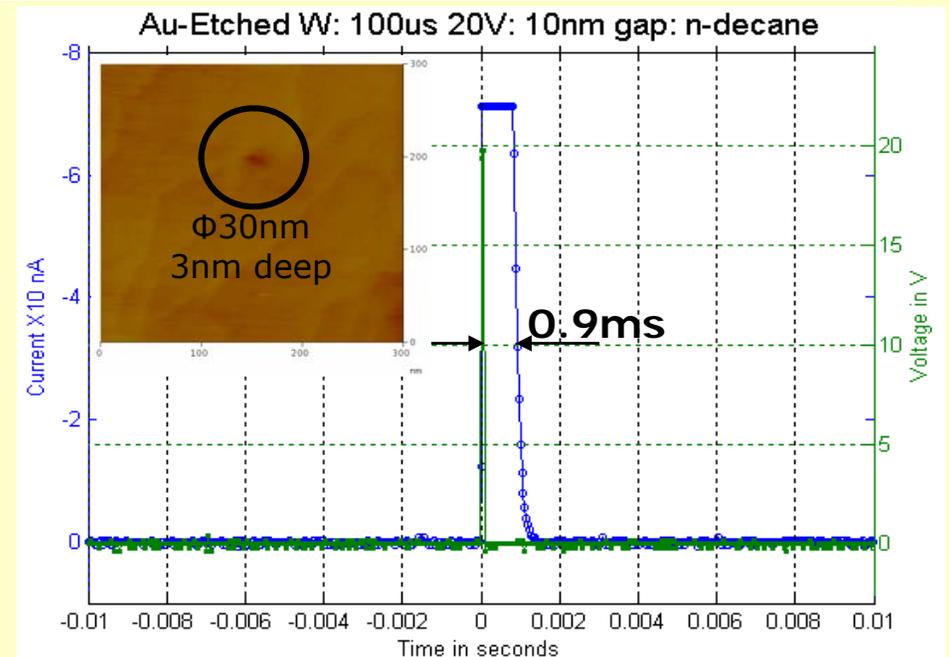
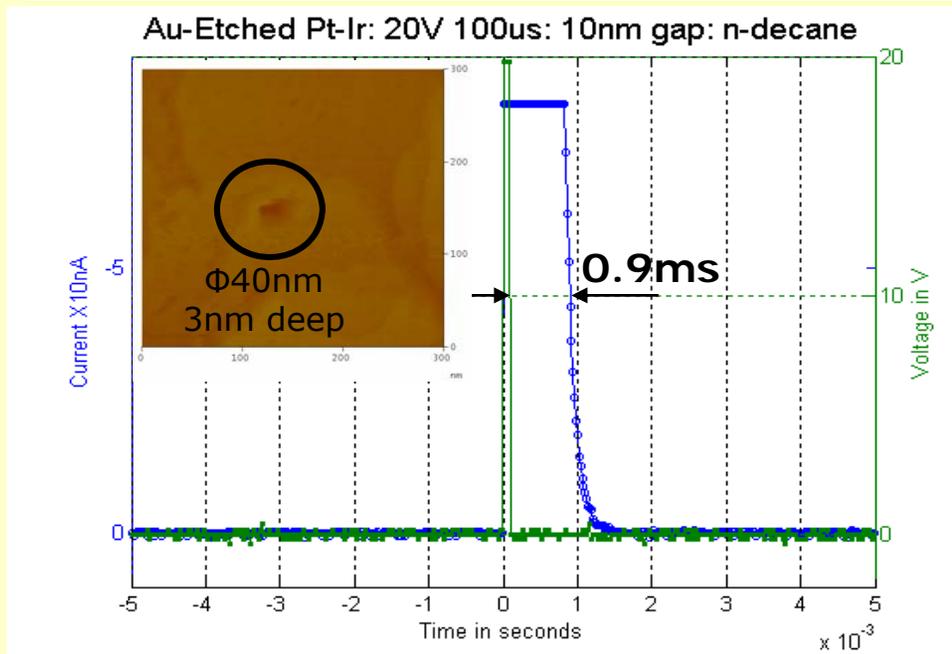


# Paschen curves in sub-20nm regime



- Linear increase of the breakdown voltage with increasing distance in the sub-20nm regime
  - Paschen curves measured for both etched W and Pt-Ir tool materials were found to be similar
- In the sub-20nm region, DC breakdown behavior was measured to be independent of the electrode material

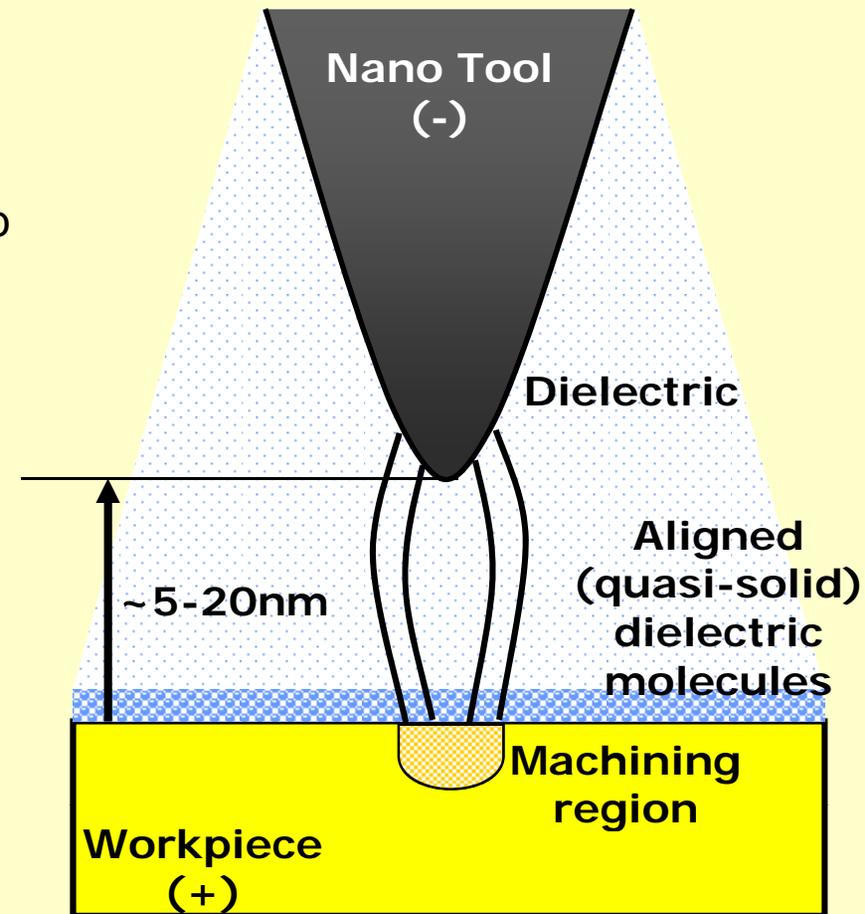
# Pulsed breakdown and machining



- As in the DC breakdown case, W and Pt-Ir show similar pulse breakdown characteristics
- There is a recovery time ( $\sim 1\text{ms}$ ) for the dielectric upon breakdown as in the case of DC breakdown, due to nanoscale confinement
- Breakdown voltage depended on the net energy available  
→ The speed of the EPL may depend on how fast the dielectric recovers its strength

# Nano-EM process mechanism

- **Process mechanism:** Increase in electric field leads to → the migration of gold molecules from atomic steps into the gap → phase change of n-decane from liquid to gaseous state and ionization → enhancement of electric field due to space charges → decrease in the gap strength and breakdown
  - Breakdown and machining at the nanoscale is greatly influenced by the tool-dielectric-workpiece interface
  - In a recent study<sup>1</sup>, water in the presence of an interface, behaved like a *solid* at the nanoscale
  - In EPL, such an interface is provided by the workpiece surface
- Hence the breakdown field strength ( $\sim 1\text{V/nm}$ ) was measured to be *two orders of magnitude* higher than macro and micro scale breakdown fields



**Proposed physical model**

<sup>1</sup> Phys. Rev. Lett. 96, 166103 (2006).

# Manufacturing process model

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- An energy balance approach was used to predict the field strength required for breakdown

- Energy required for phase change and ionization of n-decane molecules

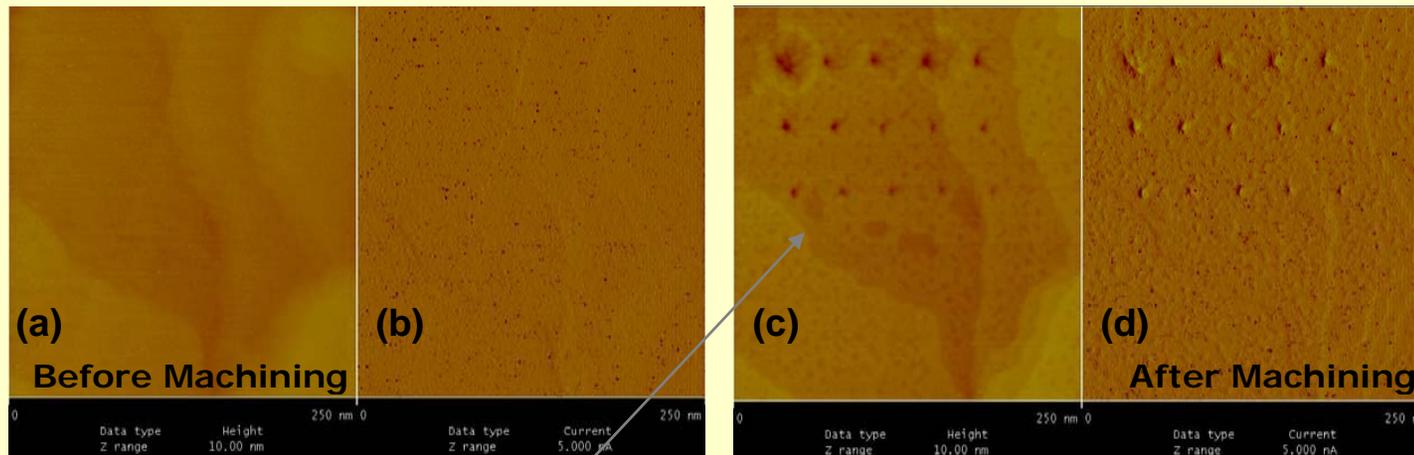
$$E_{dec} = \left( H_{dec}^{vap} + nN_A E_{dec}^{ion} \right) \left( \frac{V_{gap} \rho_{dec}}{V_{dec}^{mol}} \right)$$

- External energy input from the applied bias between the tool and workpiece

$$E_{inp} = (Vt) \left( \frac{6.2 \times 10^{-6}}{\phi + \mu} \right) \left( \frac{\mu}{\phi} \right)^{\frac{1}{2}} \left( \frac{V}{h} \right)^2 \exp \left( -6.8 \times 10^7 \times \phi^{1.5} \times \frac{h}{V} \right)$$

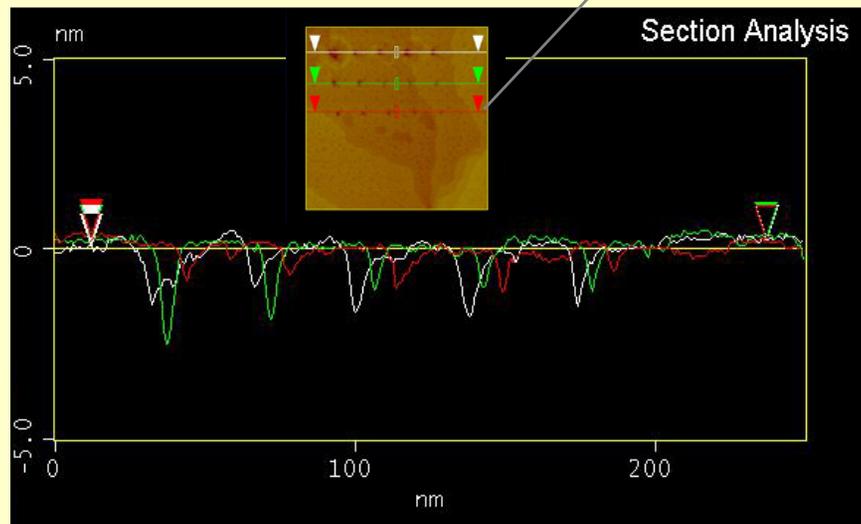
- The model predicts a breakdown field strength of **1.25V/nm** for 5% ionization coefficient
- Comparison of the experimental data and model predictions suggest about **25%** enhancement in field strength primarily due to space charges

# Array Machining: Sheared Pt-Ir tips



Figures (a) & (b) show the constant height and constant current mode STM scans of the atomically flat gold surface before nano-EM machining and (c) & (d) show the surface after machining

- ❖ 15 Features machined
- ❖ Mechanically sheared Pt-Ir tip used
- ❖ Machining conditions:
  - 3200 mV, 1 second**
- ❖ Scan conditions: 100 mV bias, 1 nA tunneling feedback current

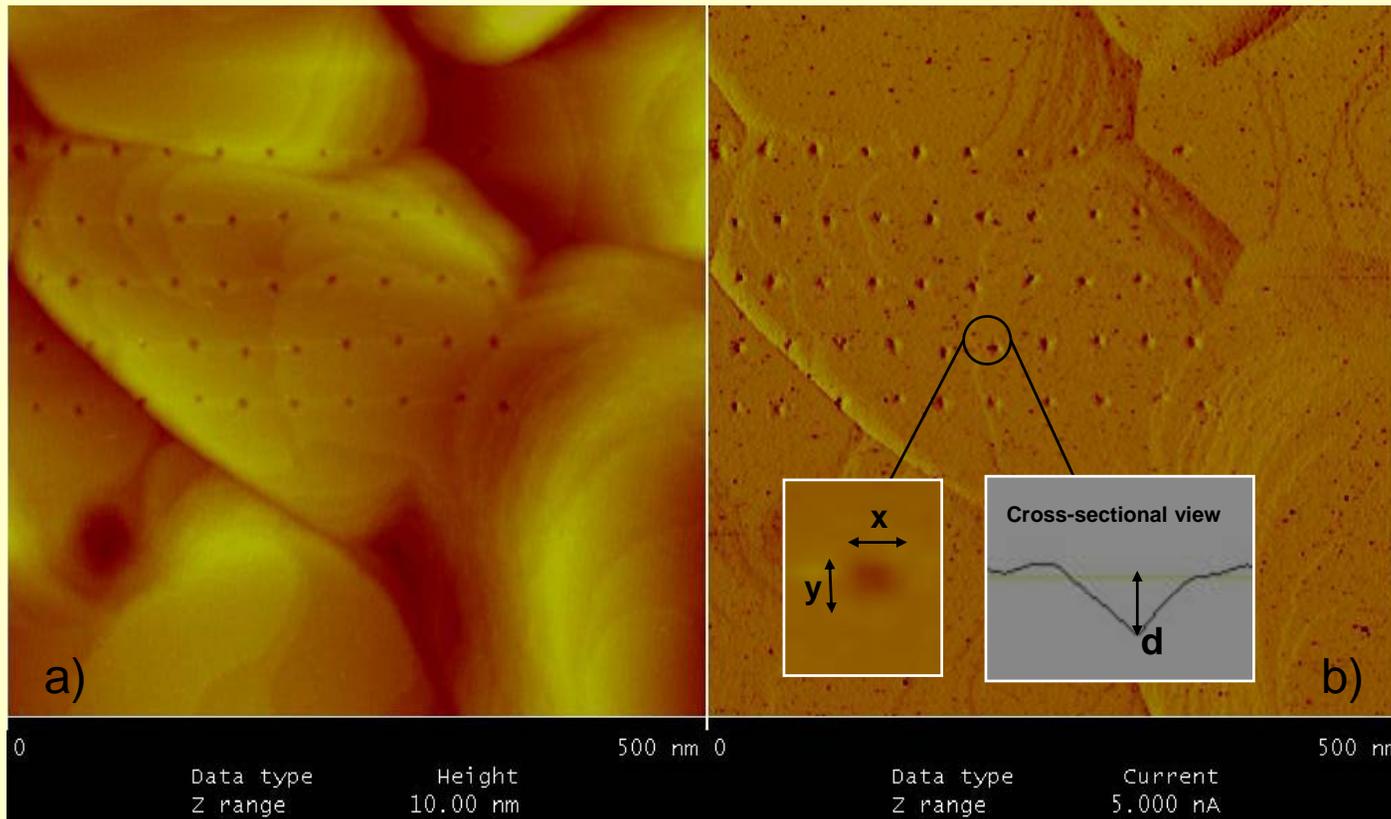


***Machined features' variation***  
X-dimension:  $8.6 \pm 1.39$  nm  
Y-dimension:  $9.2 \pm 1.68$  nm  
Depth:  $1.2 \pm 0.37$  nm

- Good consistency in machining observed
- Considerable tip wear noticed after machining
- Cross-section shows the tip wear during machining

Figure shows the cross-sectional profile of the machined features shown in the Figure above

# Array Machining: Etched Pt-Ir tips



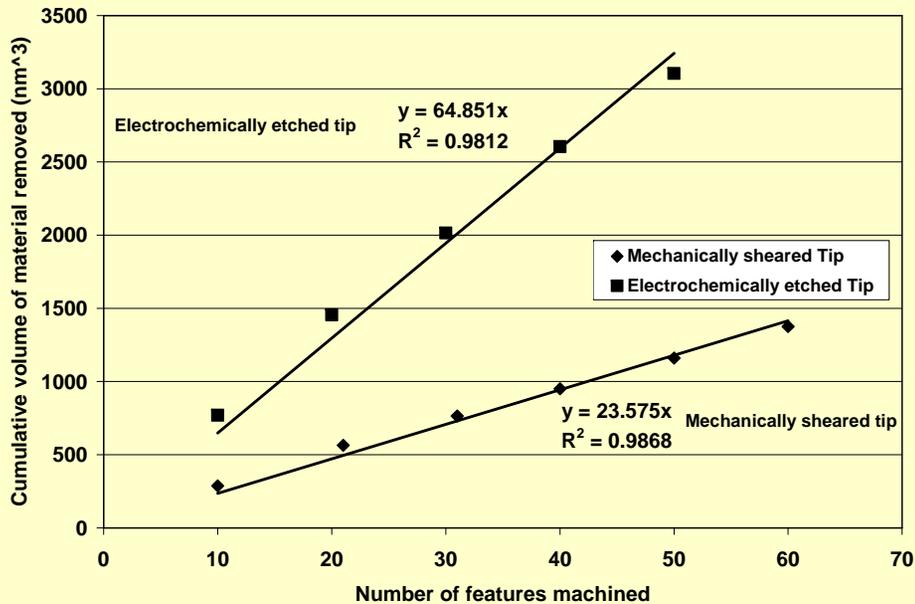
- ❖ 50 Features machined
- ❖ In-house etched Pt-Ir tip used
- ❖ Machining conditions:  
**3200 mV, 2 seconds**
- ❖ Inset description of features:  
 $x, y$  – from topography  
 $d$  – from cross-sectional view
- ❖ Scan conditions: 100 mV bias, 1 nA tunneling feedback current

Figure shows the constant height mode (a) and constant current mode (b) STM scans of the atomically flat gold surface after nano-EM machining

- Excellent consistency in machining observed
- Repeatability is very good as compared to sheared tips
- Same tip can machine up to 150 features in a single cycle

# Array machining: Comparison

Cumulative volume of material removed vs Number of features machined

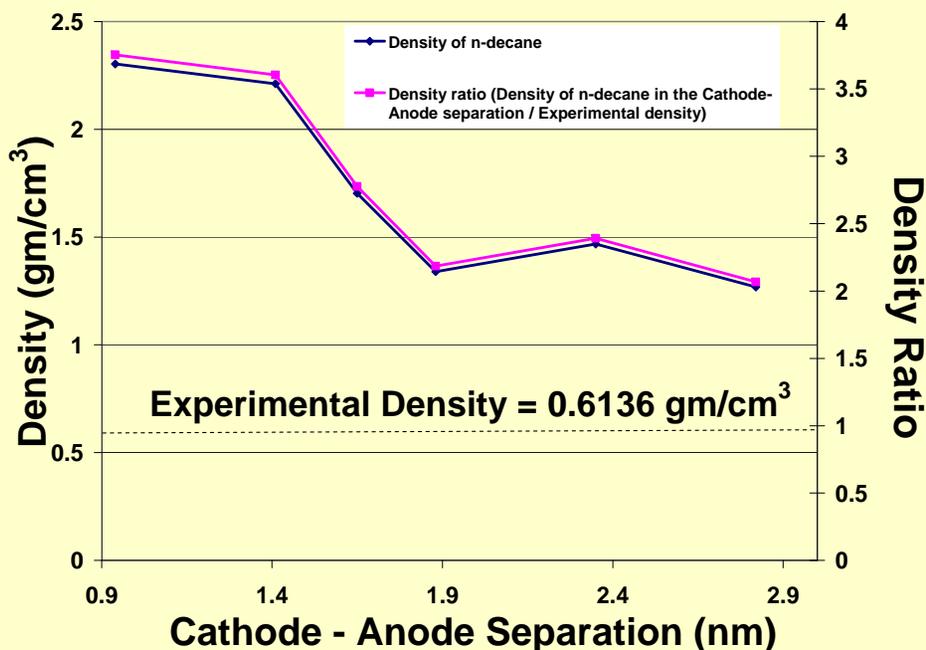


Type of Tip used	Mechanically sheared Pt-Ir tip		Electrochemically etched Pt-Ir tip	
Feature Dimension	Mean value (in nm)	Spread from mean	Mean value (in nm)	Spread from mean
X ± Standard deviation	8.724 ± 1.543	18%	8.790 ± 1.030	12%
Y ± Standard deviation	10.352 ± 1.320	13%	8.854 ± 0.880	10%
Depth ± Standard deviation	0.403 ± 0.167	42%	0.745 ± 0.250	34%

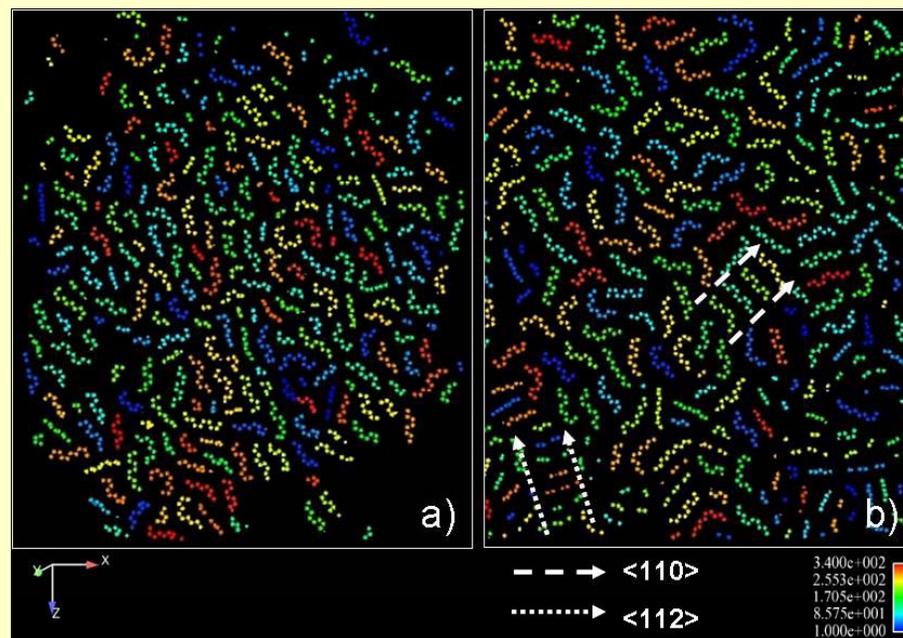
- Considerable difference (~ thrice) in the amount of material removed between the two tips used
- Etched tips do remove lot of material as compared to sheared tips because of their tip profile under same machining conditions
- Etched tips produce deeper (Z-direction) features as they are sharper than sheared tips

# Modeling results

Collaborator: Dr. Douglas E. Spearot, University of Arkansas



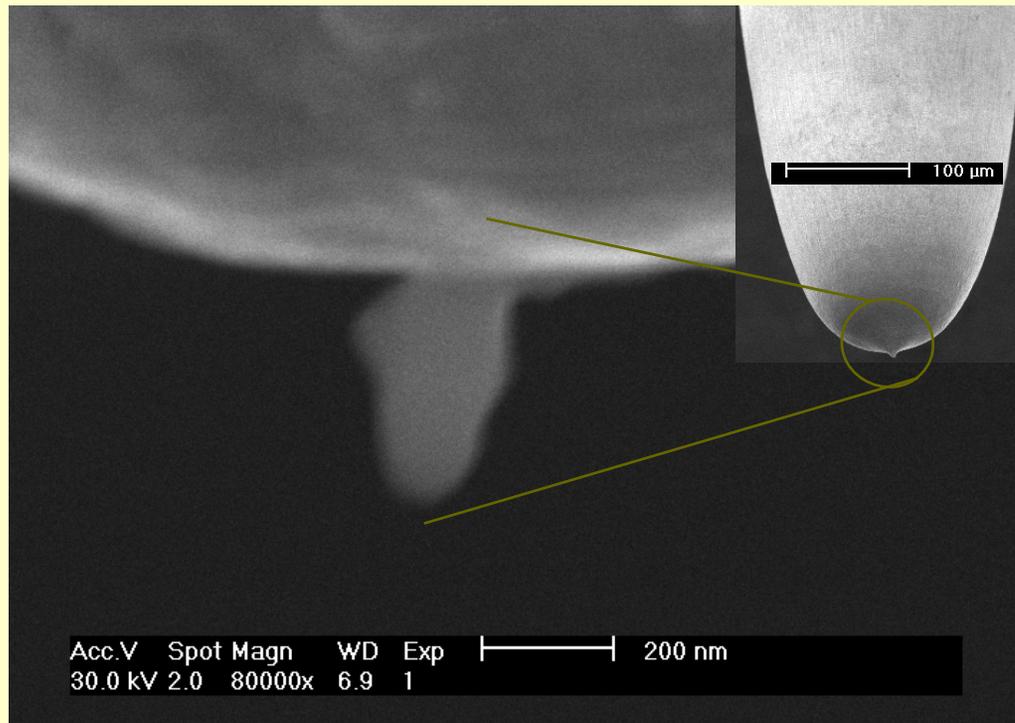
Density and density ratios of n-decane molecular medium for different cathode-anode separations



Top-view of one of the layers of n-decane chains a) before and b) after dynamics clearly showing the preferred orientation of chains after dynamics. The chains are colored based on their chain number

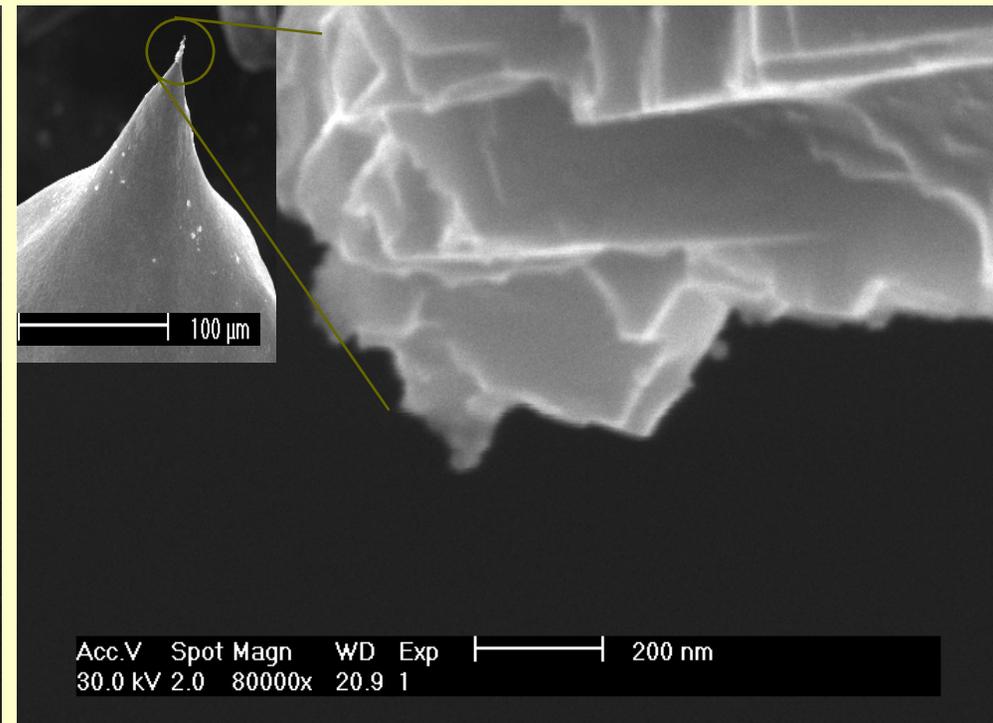
- Up to four-fold increase in the density of n-decane molecular medium (as compared with experimental density) under mechanical boundary conditions
- Top view shows highly-ordered “quasi-solid” behavior and organization of n-decane medium with preferred orientation along certain crystallographic directions

# SEMs of commercially available & In-house etched Pt-Ir tips



SEMs of commercially available etched Pt-Ir (80-20%) tips

*\*Obtained from: Agilent Technologies*

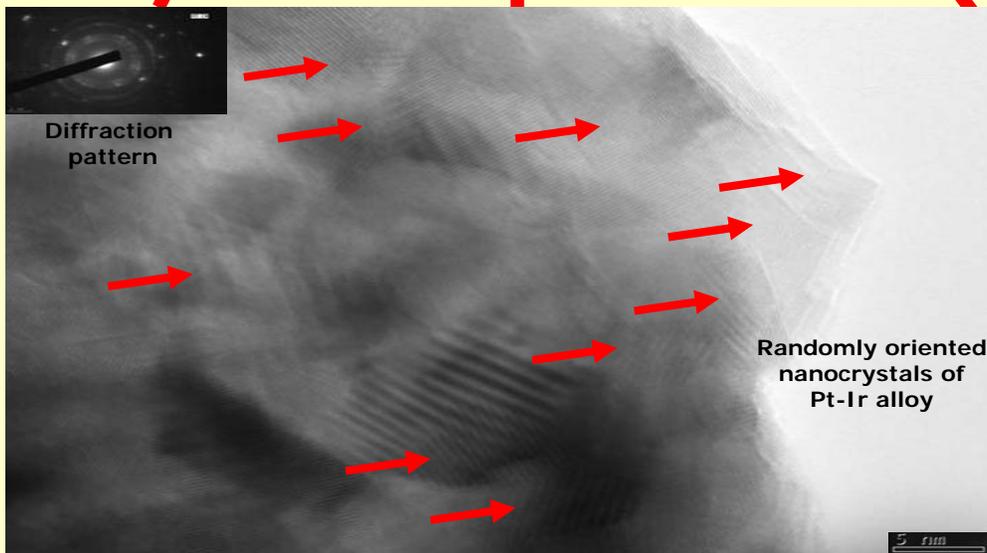


SEMs of in-house electrochemically etched Pt-Ir (80-20%) tips

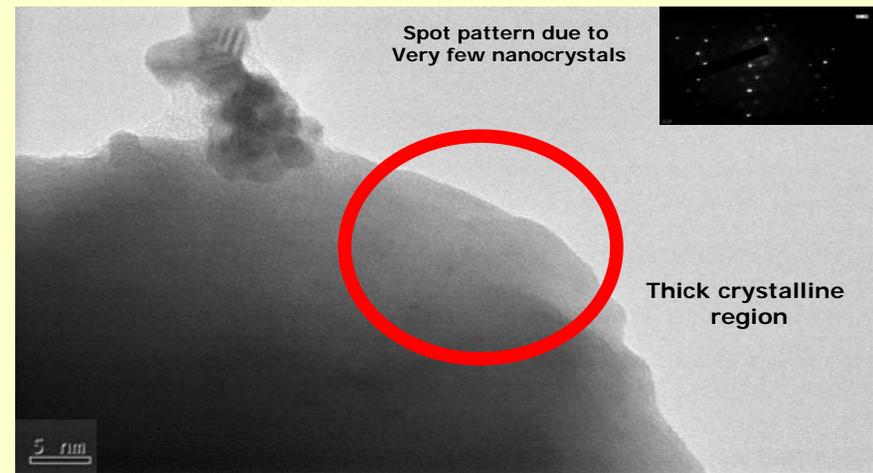
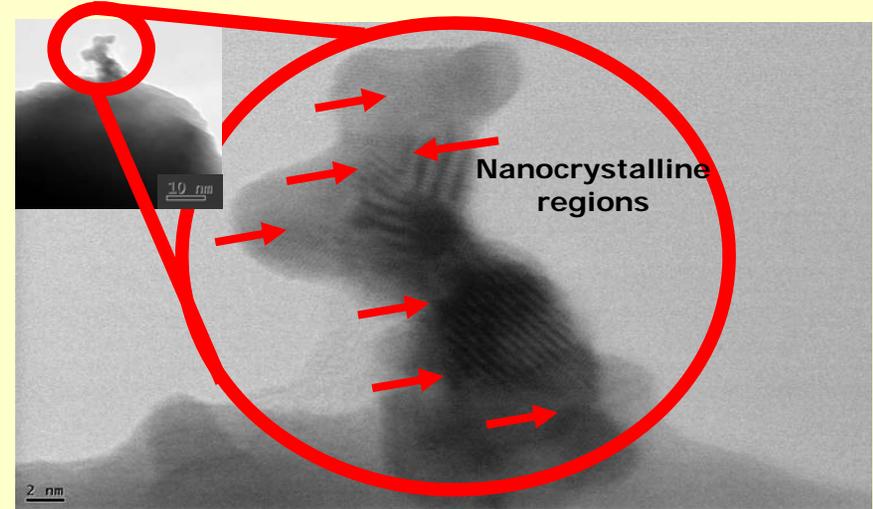
- Commercially available tips are “blunt” as compared to in-house etched tips
- At MMRL, in-house tips’ etching efficiency is around **80%** in obtaining tips of quality “1”

# HRTEM Studies of Etched Pt-Ir Tips

Before Machining

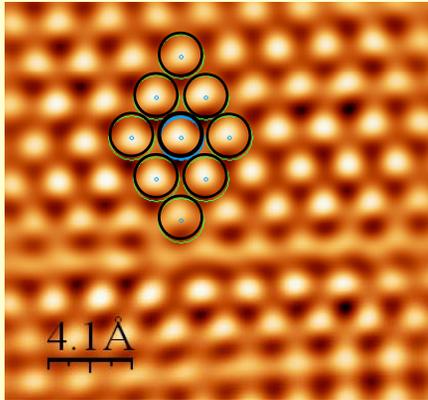


After Machining 20 features

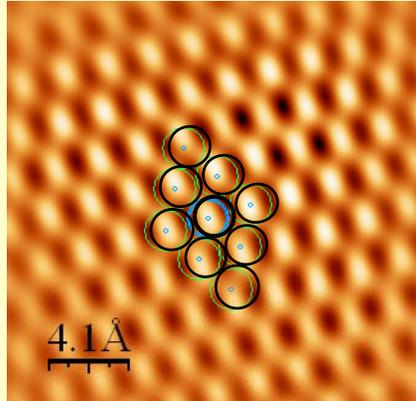


# Preliminary studies of nano-strain in HOPG

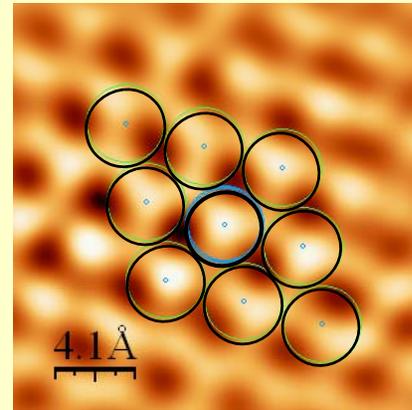
Before machining  
 $a = 0.235 \text{ nm}$



Near to feature boundary  
 $a = 0.226 \text{ nm}$

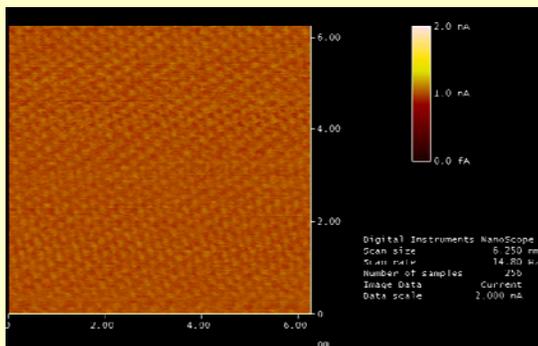


Machined feature's boundary  
 $a = 0.454 \text{ nm}$

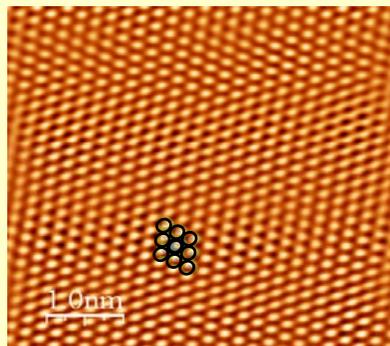


- ✍ Mode: Interleave Mode
- ✍ Substrate: Highly Oriented Pyrolytic Graphite (HOPG)
- ✍ Tip: Mechanically sheared W tip
- ✍ Bias voltage: 10,000 mV
- ✍ Machining Distance: 4.3 nm
- ✍ Dielectric: Air

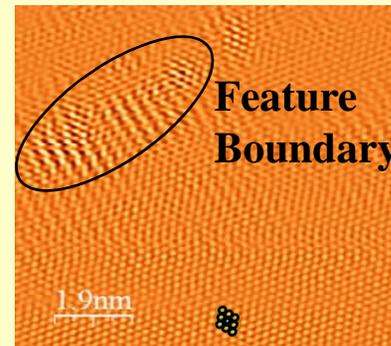
Atomic Resolution Image



Before Machining  
 $a = 0.23 \text{ nm}$



Complete Lattice disregistry  
near feature boundary



- ✍ Mode: STM range machining
- ✍ Substrate: HOPG
- ✍ Tip: Mechanically sheared W tip
- ✍ Bias voltage: 5,000 mV
- ✍ Machining Duration: 0.25 seconds
- ✍ Dielectric: n-decane

# Driver needs where *in situ* and *ex situ* sensing and measurements are critical

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- Demonstration of a molecular device application using 2D and 3D EPL
- Measuring surface integrity, tolerances and reproducibility and repeatability of machined features
- Understanding the role of dielectric medium organization in the nano-tool-workpiece interface and in situ tool wear
- Improving EPL machining speed from 2Hz (instrumentation limitation) to about 1kHz
- EPL scale-up to perform parallel machining of features, similar to IBM Millipede™ platform

# Conclusions

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- EPL enabled studies of the breakdown of liquid dielectrics across user-defined gaps in the nanometer regime
- Space charges play a dominant role in the nanoscale dielectric liquid breakdown behavior
- A linear scaling of the breakdown voltage with distance (sub-20nm) helps in easy power requirement predictions
- Liquid dielectric breakdown was found to be independent of cathode material work-functions at least between W and Pt-Ir, simplifying tool design
- Current-displacement curves enable *in situ* and in line tool quality monitoring for EPL and have been adapted for evaluation of STM tips
- Repeatability of the process shows good manufacturing scalability prospects

# Publications and patents

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- **Publications**

- "In situ characterization of nano electro-machining tool and nanomanufacturing process repeatability", V. Kalyanasundaram, K.R. Virwani, D.E. Spearot, K.P. Rajurkar and A.P. Malshe, Transactions of the NAMRI, Accepted for publication (2008).
- "Understanding behavior of dielectric molecular medium and machining-induced zone in nanoscale electro-machining", V. Kalyanasundaram, K.R. Virwani, R. Guduru, D.E. Spearot, A.P. Malshe and K.P. Rajurkar, CIRP Annals – Manufacturing Technology, submitted (2008).
- "Understanding sub-20nm Breakdown Behavior of Liquid Dielectrics", Virwani K. R., Malshe A. P. and Rajurkar K. P., Physical Review Letters, 99, 017601-1-4 (2007).
- "Understanding Dielectric Breakdown and Related Tool Wear Characteristics in Nanoscale Electro-Machining Process", Virwani, K.R., A.P. Malshe and K.P. Rajurkar, CIRP Annals, 56, 1, 217 (2007).
- "Current displacement (I-Z) spectroscopy based characterization of nanoscale electric discharge machining (nano-EDM) tools", Virwani K. R., Rajurkar K. P. and Malshe A. P., International Journal of Nanoengineering and Nanosystems, 220, 1, 21 (2006).
- "Investigation of Nanoscale Electro Machining (nano-EM) in Dielectric Oil", Malshe A. P., Virwani K. R., Rajurkar K. P. and Deshpande D. C., CIRP Annals, 54, 1, 175 (2005).

- **Patent**

- "Method, System and Apparatus for Nanoscale Electric Discharge Machining or Nano-EDM" (pending)

# Outreach

- Offered a course on 'SPM based Nanomanufacturing' during Spring 2006
- Worked with REU students on various projects using SPM during summer 2005, 2006 & 2007
- High school field trip on 'See the Atoms' in summer 2006
- Trained students from Fayetteville High School on imaging biological membranes

