Micro/Macro Integration of Nanostructures and Nanomaterials

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The Charles Stark Draper Laboratory, Inc.

Innovative Engineering for Over 75 Years

Independent, not-for-profit

Dedicated to

- **Applied research and development**
- **Technology transfer**
- **Advanced technical education**

Divested from MIT in 1973

Headquarters in Cambridge, Mass.

- **Site offices in Houston; Huntsville; Tampa Bay; and Washington, D.C.**

Revenues exceed $420 million

Approximately 1400 employees

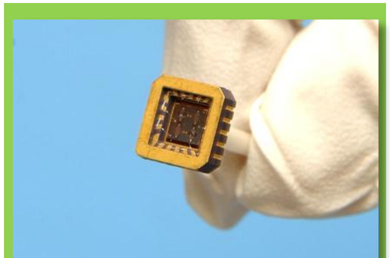
- **65% technical staff**
- **$^2/_3$ with advanced degrees**

Photo credit: John Earle

Draper's Evolution

From the Birthplace of Inertial Navigation to Advanced Engineering R&D

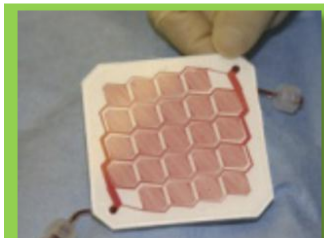
Guidance, Navigation & Control



MEMS

Robotics

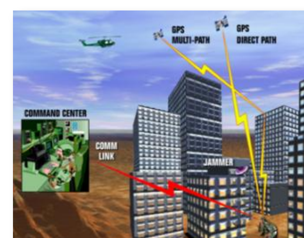
Fault Tolerance



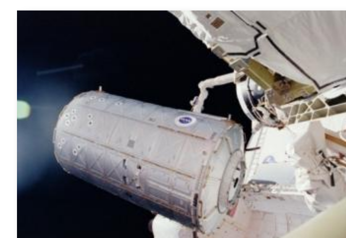
Biomedical Engineering

Microsystems

Autonomous Systems

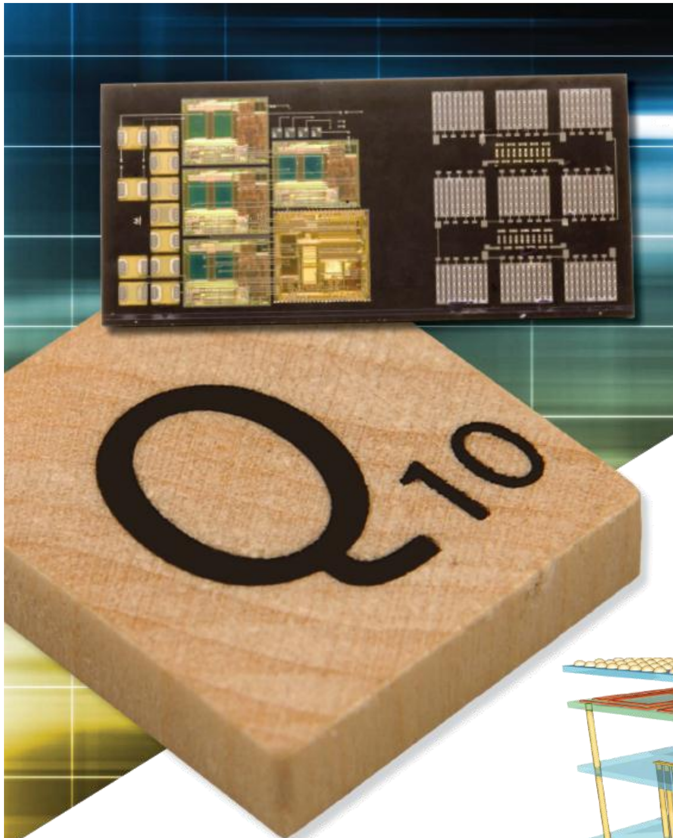


Distributed Communications & Control

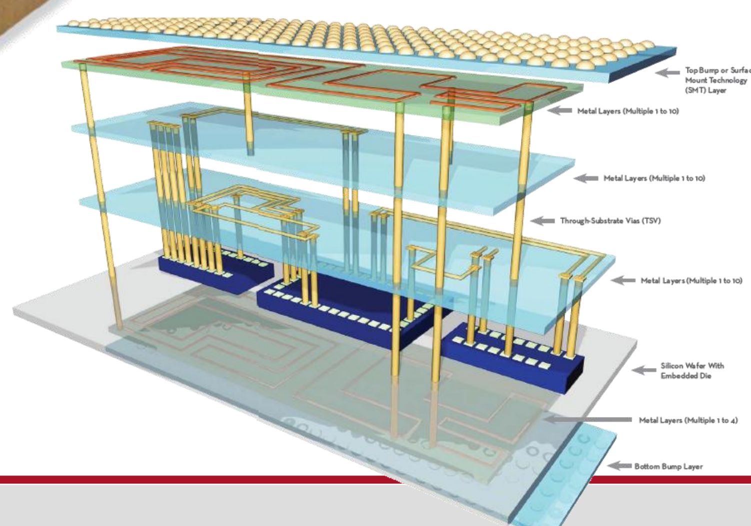


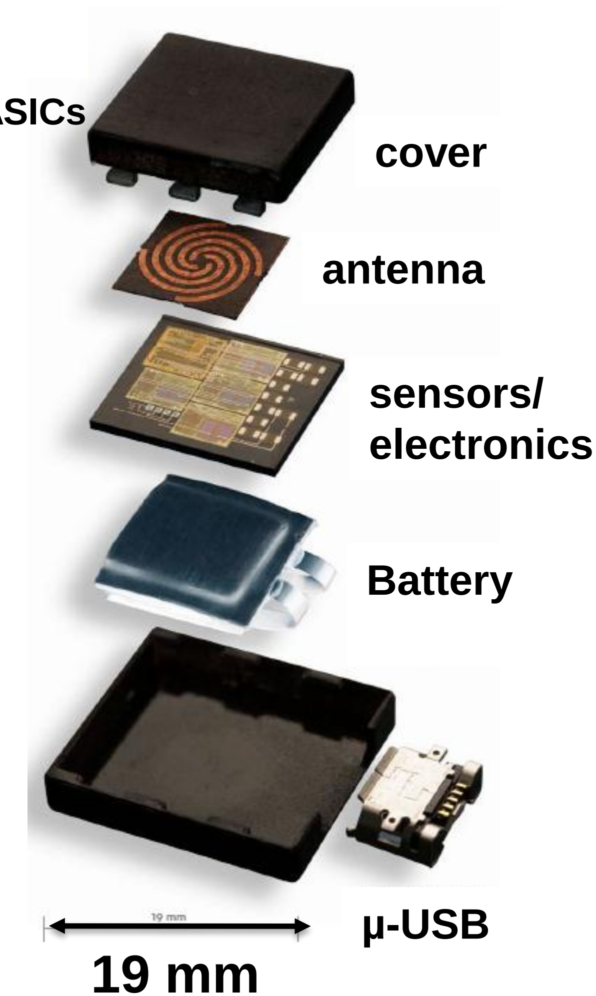
Critical System Design

Vanishingly Small Systems



Sensors
DSP in FPGA
Large Value Passives
Mixed Signal and Structured ASICs
Thermal Management
High Efficiency RF PA
Algorithms
i-UHD Electronics Packaging
Frequency Reference
RF MEMs
Antennas
Power Source
Waveforms/Protocols





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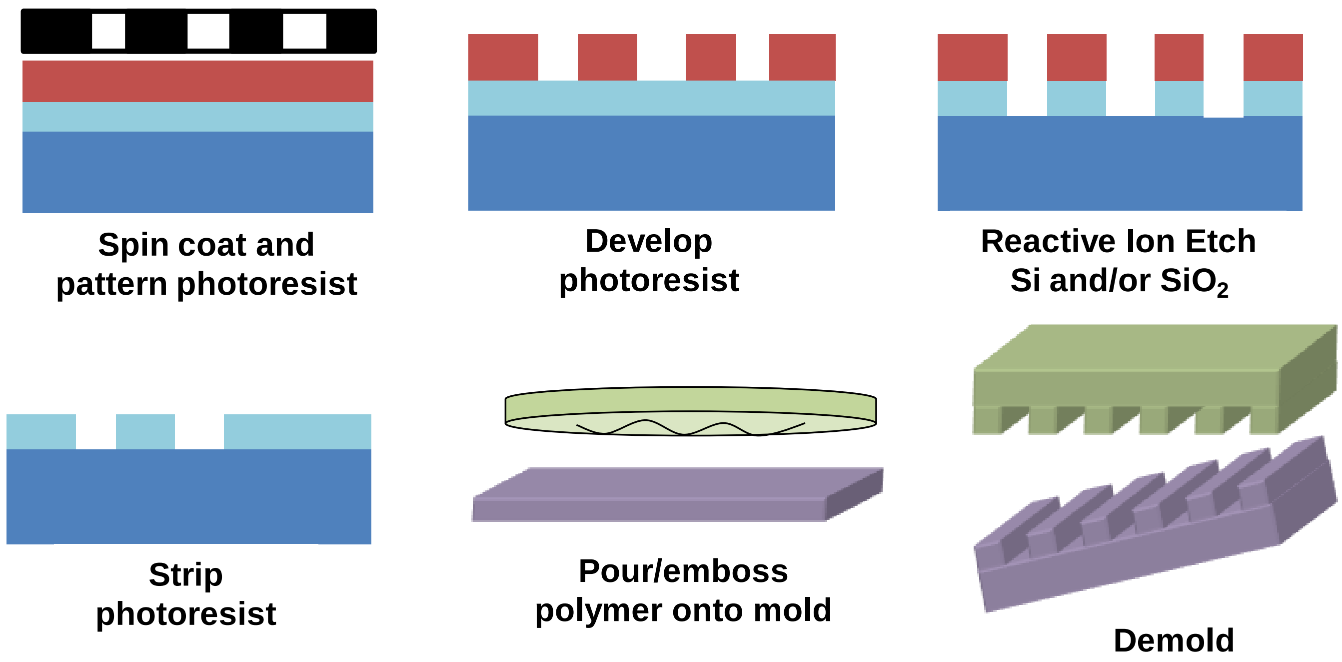
Nanotechnology at Draper

- Mainly in MEMS and Biomedical Areas (some robotics)
- Typically, nanostructured element or nanomaterials integrated with MEMS device or other micro/macro system
- Extensive interactions/collaborations with universities
- Areas:
  - Nanostructured polymers
    - tissue engineering, gecko adhesion
  - Nanostructured metal films
    - chem/bio sensors
  - CNT integration with MEMS
    - Applications: rotary MEMS (*e.g.* gyroscope, …)

Nanostructured Polymers

Typical process



Feature sizes: few microns → ~50 nm

- optical contact litho (~400 nm), e-beam litho, interference litho, diblock copolymers, …
- *n.b.* shown below are ~800 nm feautures, but exploring finer topography as well

Molds: Si, SiO_2, electroplated Ni, …

Wide variety of polymers

Also investigated injection nanomolding with Si inserts

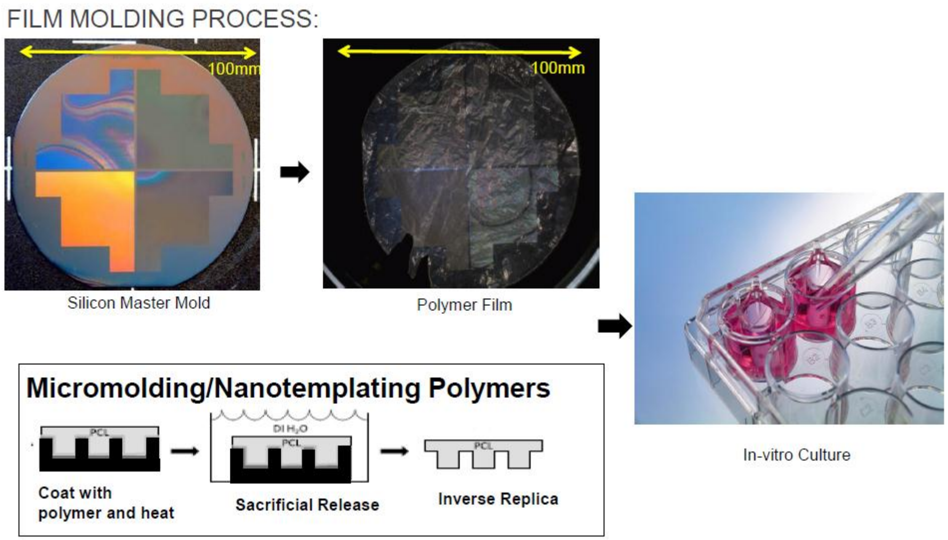
Tissue Engineering

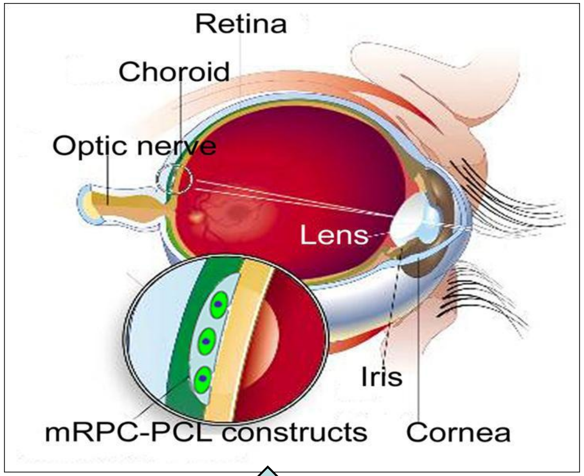
- ***Long-term goal***: Micro/nanotopography to cue stem cell growth/behavior for proper function as replacements in existing organs and/or in artificially-engineered organs
  - *e.g.* **retinal cells** for macular degeneration, retinitis pigmentosa
  - *e.g.* **renal tubule cells** for kidney disease
- ***Current Research***: Create synthetic cellular environments to attempt to replicate native environment of cells
  - Investigate cell type-specific responses, such as alignment, elongation and cell-cell junction formation in a physiologically realistic environment
  - Contribute to research surrounding cellular superstructure formations and stem cell differentiation as well as to the ever-growing fields of tissue engineering and regenerative medicine

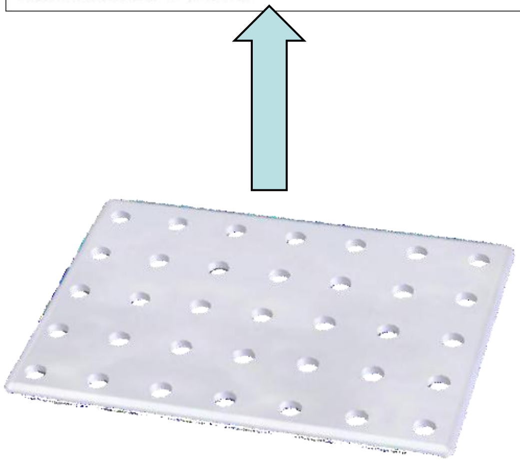
Foundation Fighting Blindness℠
DISCOVERY EYE FOUNDATION
The Lincy Foundation

Retinal stem cells cultured on polycaprolactone thin film

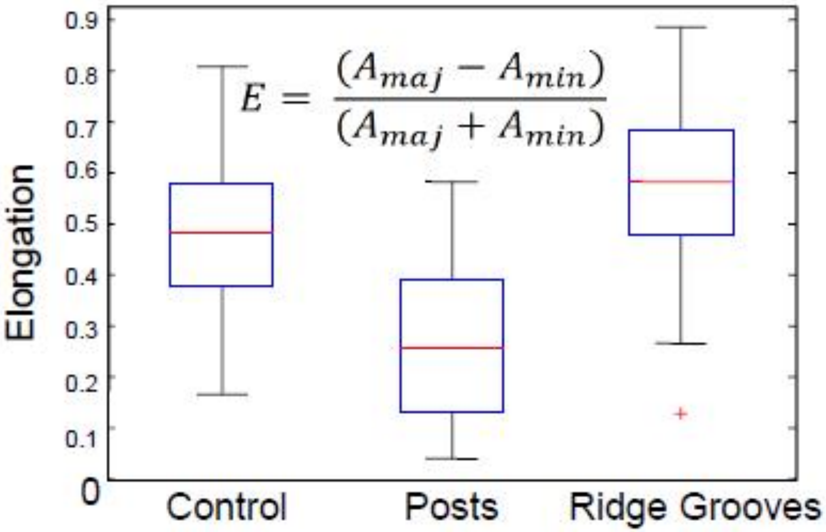
-Thin for subretinal transplantation (<10um)
-Can deliver large population of cells
-Provide cell guidance with submicron cues
-Relatively stiff for surgical manipulation
-Flexible for curvature
-Biocompatible/biodegradable in sub-retinal space

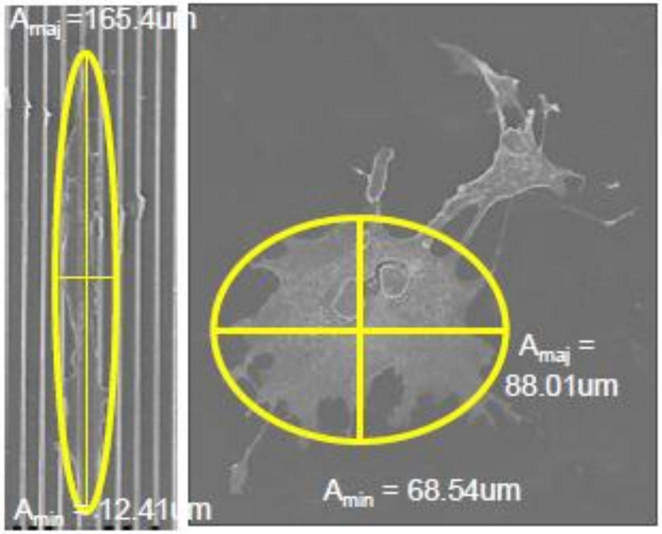


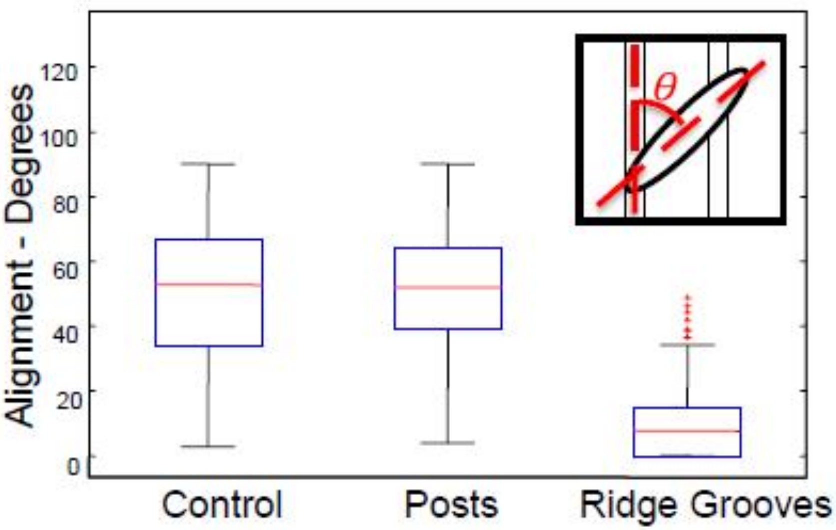


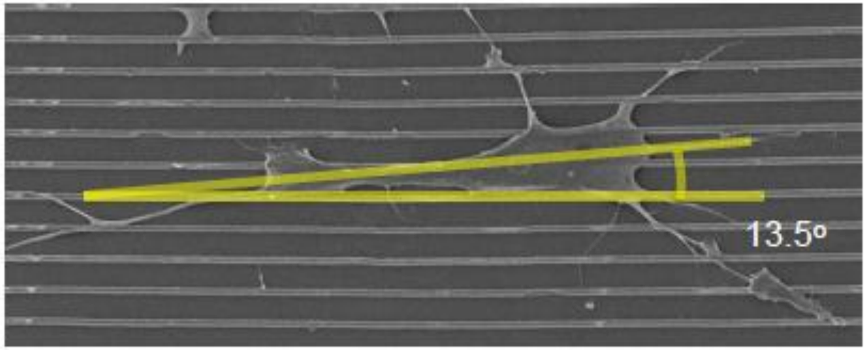


Retinal stem cell morphology response to micro/nano features









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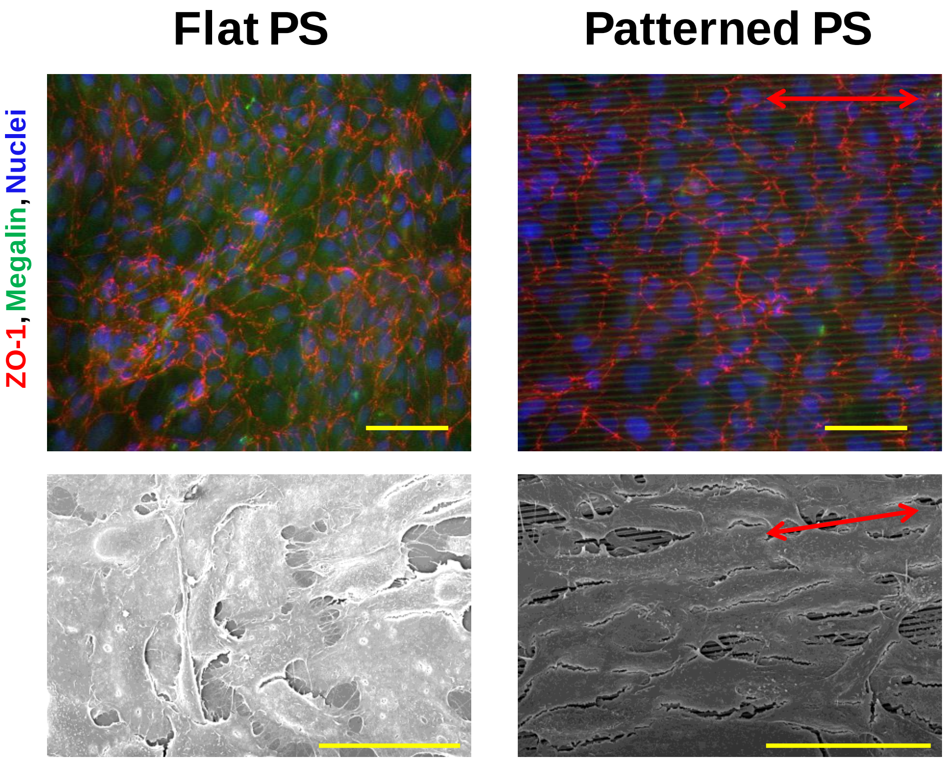
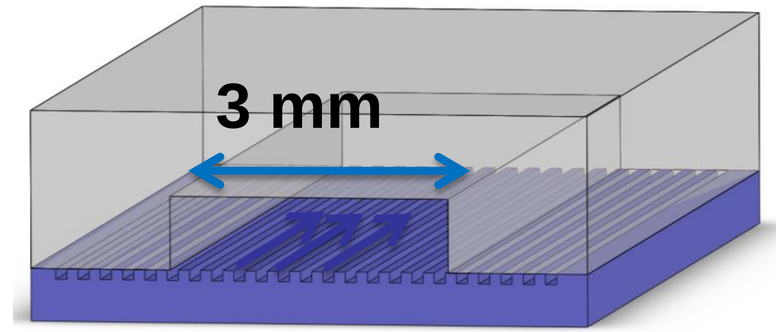
Kidney tubule cell culture



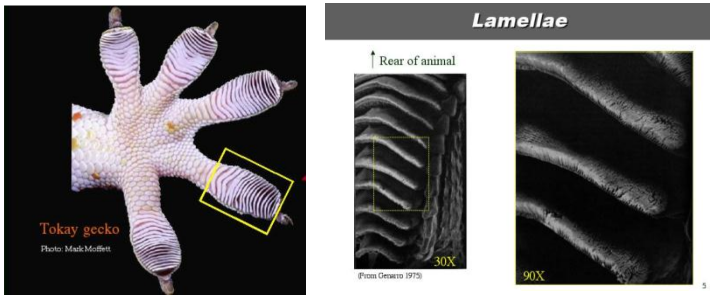


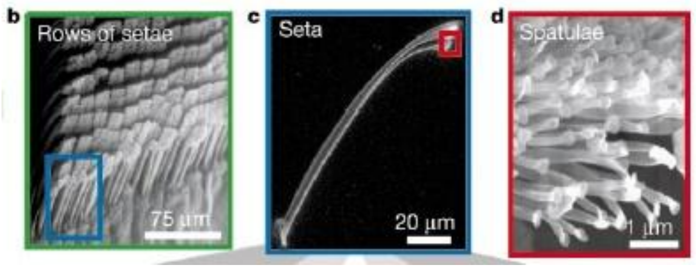
Next step: add microfluidic flow chamber to flow-induced shear stress (FSS) similar to kidney tubule environment

- **Human renal proximal tubule cells**
- **Ridge-groove features horizontal (red arrows)**
    - **0.9-1.0 µm in width.**
- **Cells align and elongate only on the patterned PS**
- **All scale bars 50 µm**

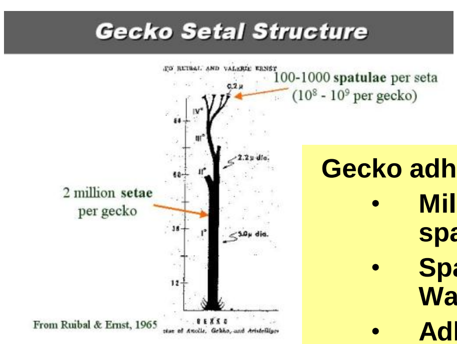
Nanopatterned Artificial Gecko Adhesive

Biomimetic adhesive (one-sided velcro)





http://www.lclark.edu/~autumn/climbing/

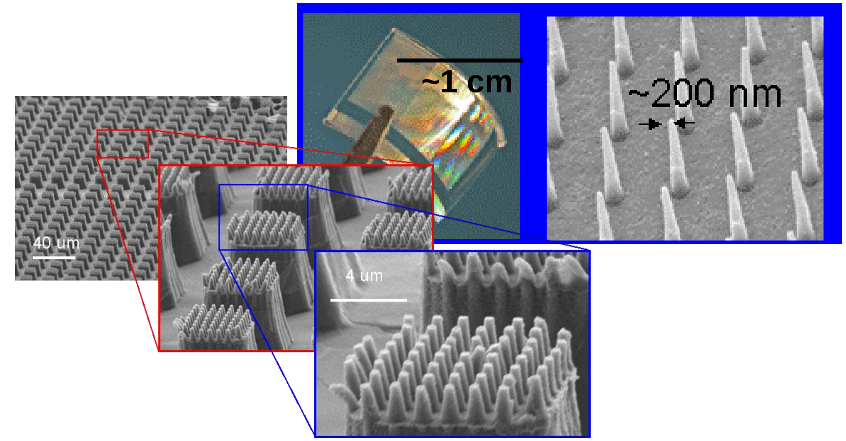


Gecko adhesion:

- Millions of tiny (~200 nm) spatulae
- Spatulae adhere by van der Waals forces
- Adheres to a variety of surfaces, wet/dry, etc.

Artificial gecko adhesive fabrication:

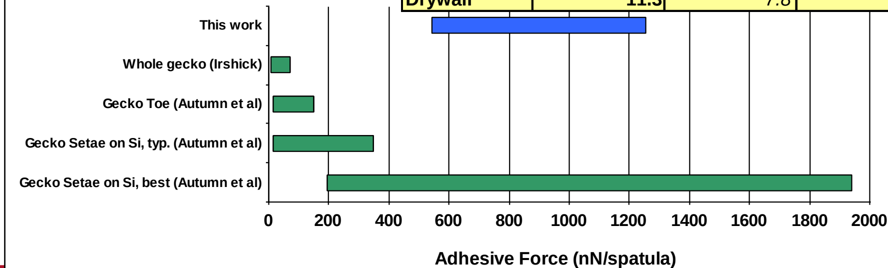
- Use nanolithography to pattern nanomolds
- Mold and release polymers



Biomimetic material adheres better than gecko

Test Surface	Roughness (um)	Adhesion (mN/mm^2) Normal	Shear
Glass	0	*332.4*	*300.9*
Al (polished)	0.7	*223.6*	*56.2*
PVC	1.5	*11.9*	*24.7*
Al (as received)	1.8	*172.6*	
Roughened Si	3.25	*93.1*	*6.5*
Al (0.120 grit)	8.1	*47.6*	
Drywall	11.3	*7.8*	

Parallel Adhesive Force Data



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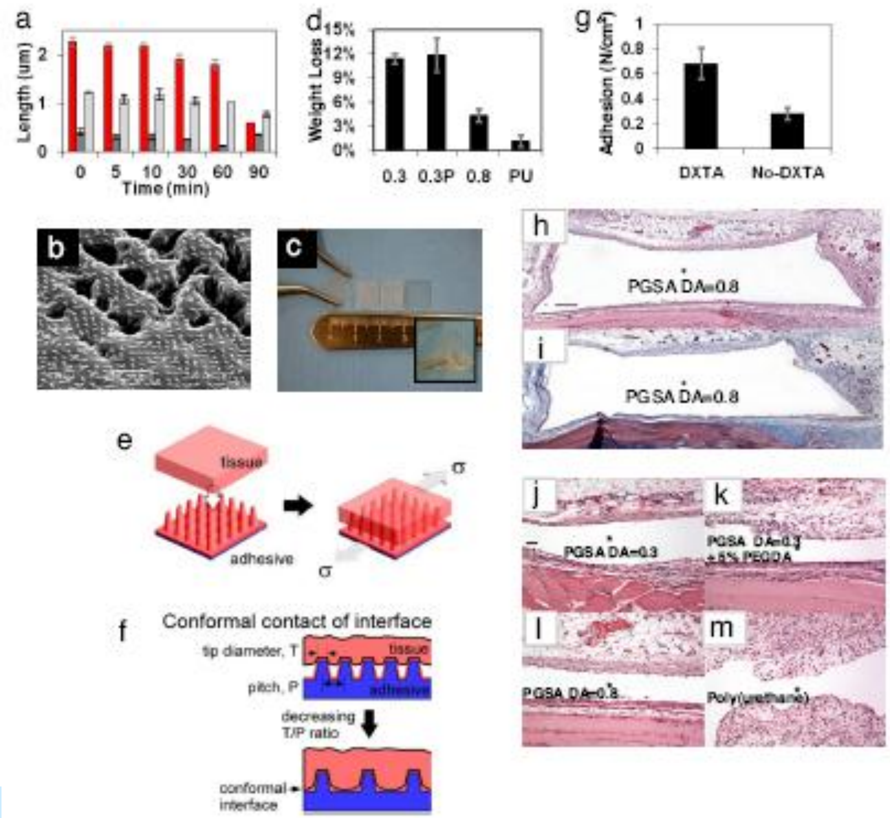
Gecko-based Medical Adhesive

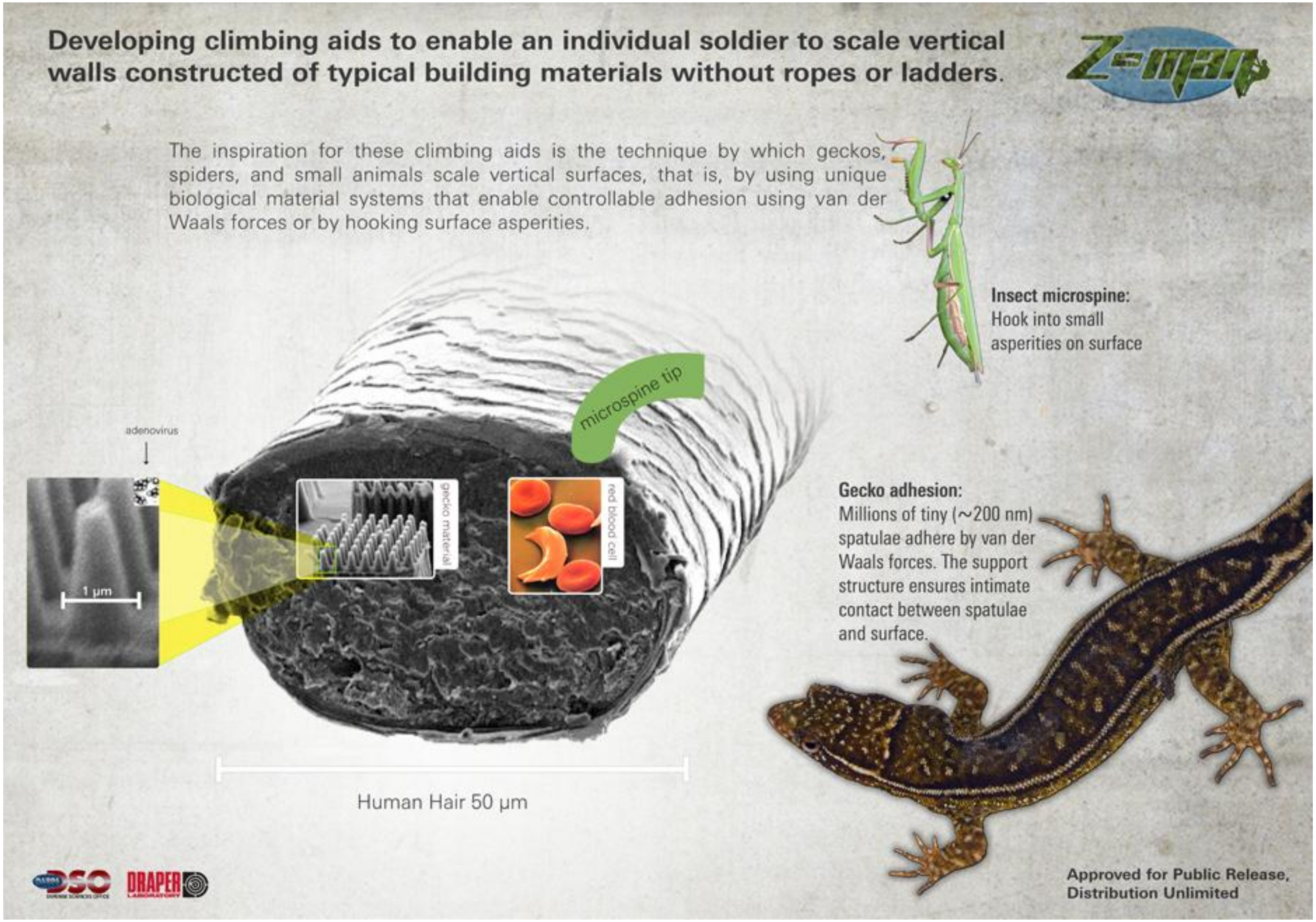
- Fabricate micro/nanostructures of biodegradable polymers
- *Functionalize surfaces of structures* to improve adhesion to tissue
- Test adhesion to tissue (porcine intestines)
- Implant into rats and observe inflammation response (~none)



Potential application to wound sealing, augmenting surgical sutures or staples

A biodegradable and biocompatible gecko-inspired tissue adhesive, A. Mahdavi *et al*, PNAS 105 2307 (2008).

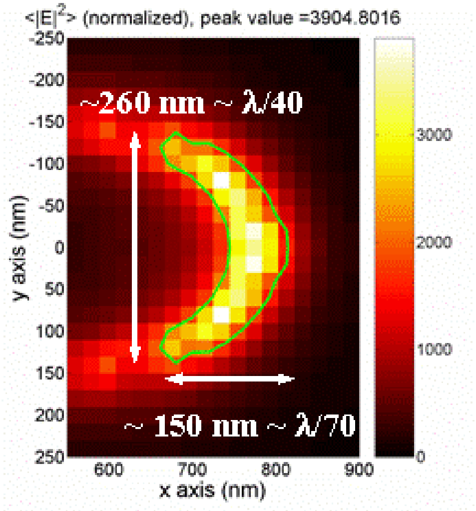
Biomimetic Adhesion (DARPA Zman)

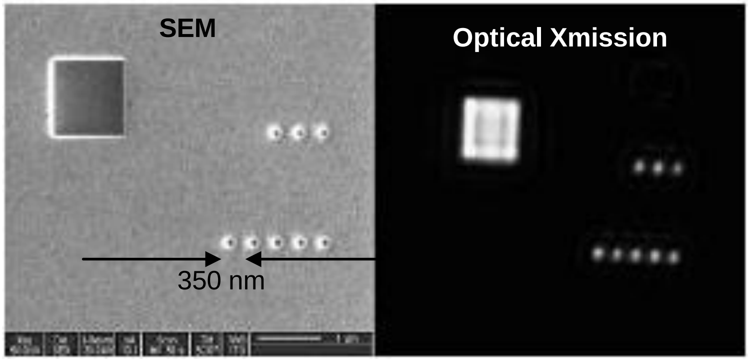


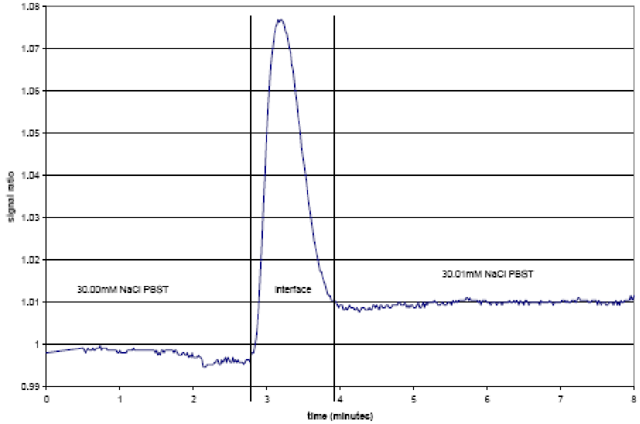
Nanostructured Metal Films

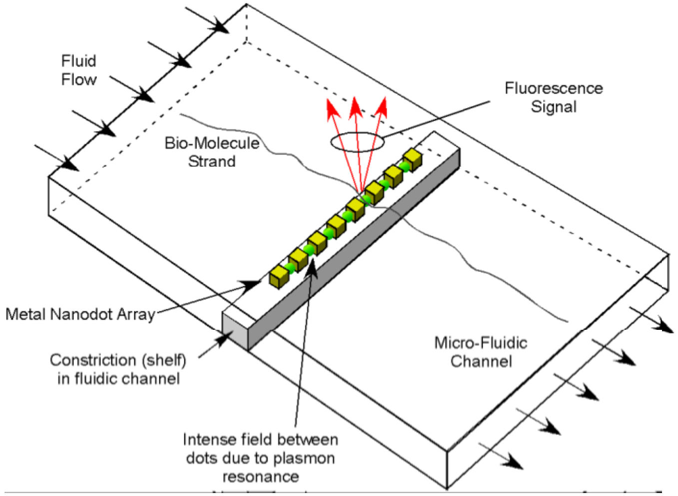
Plasmonics Phenomena and Applications

- **Plasmonic nanoantenna**
  - **DNA Sensor**
- **Extraordinary Optical Transmission (EOT)**
  - **Biosensor/Calorimeter**









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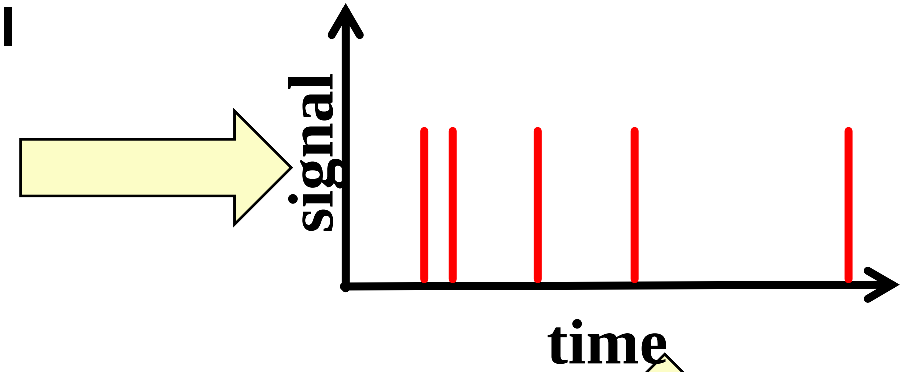
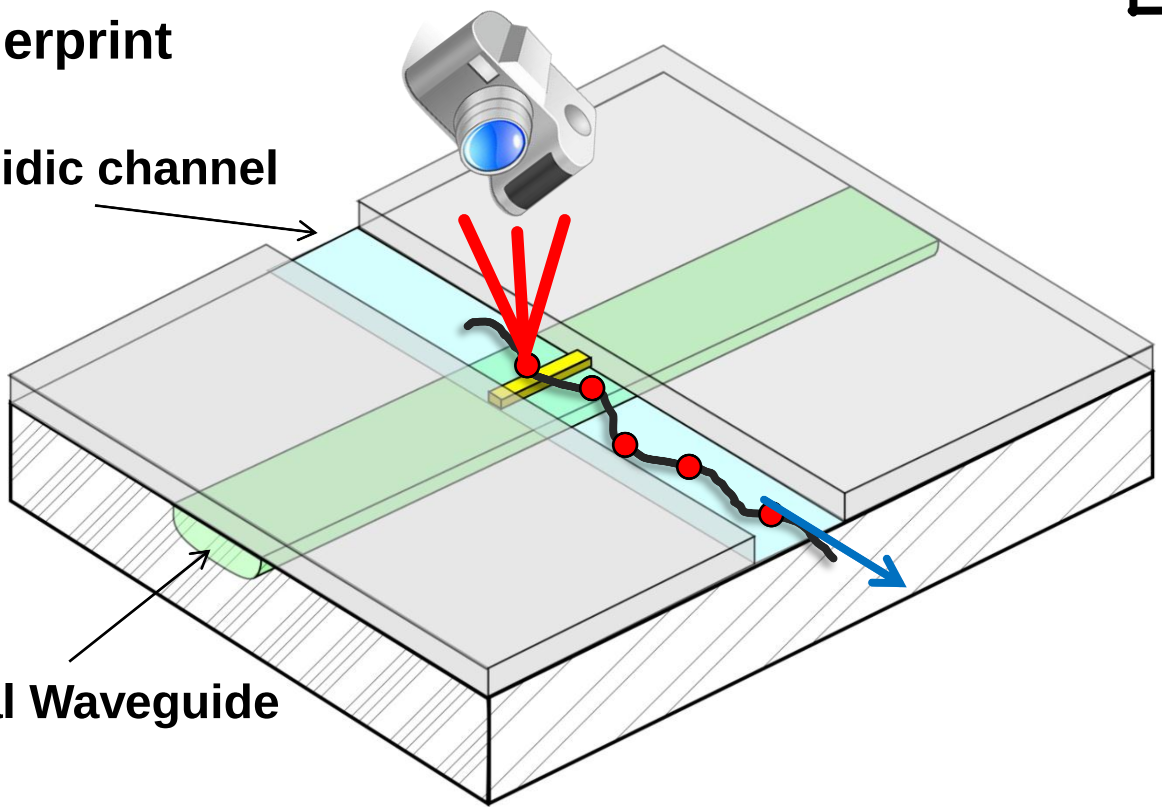
Direct Linear Analysis (DNA detection)

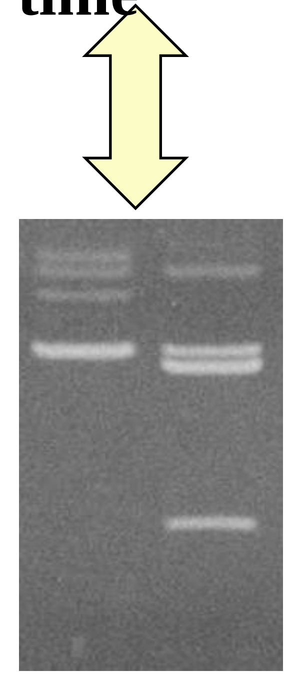
- Tagged DNA flows through channel
- Observe fluorescence with camera
- Spacing produces characteristic fingerprint



Ufluidic channel

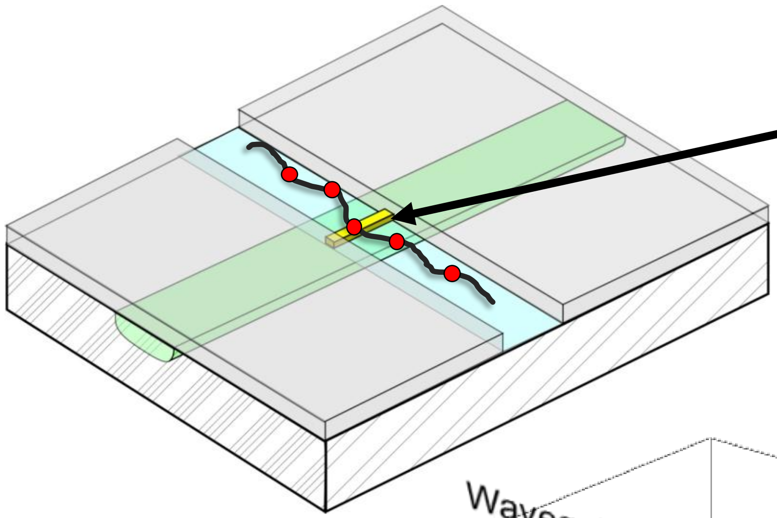


Optical Waveguide



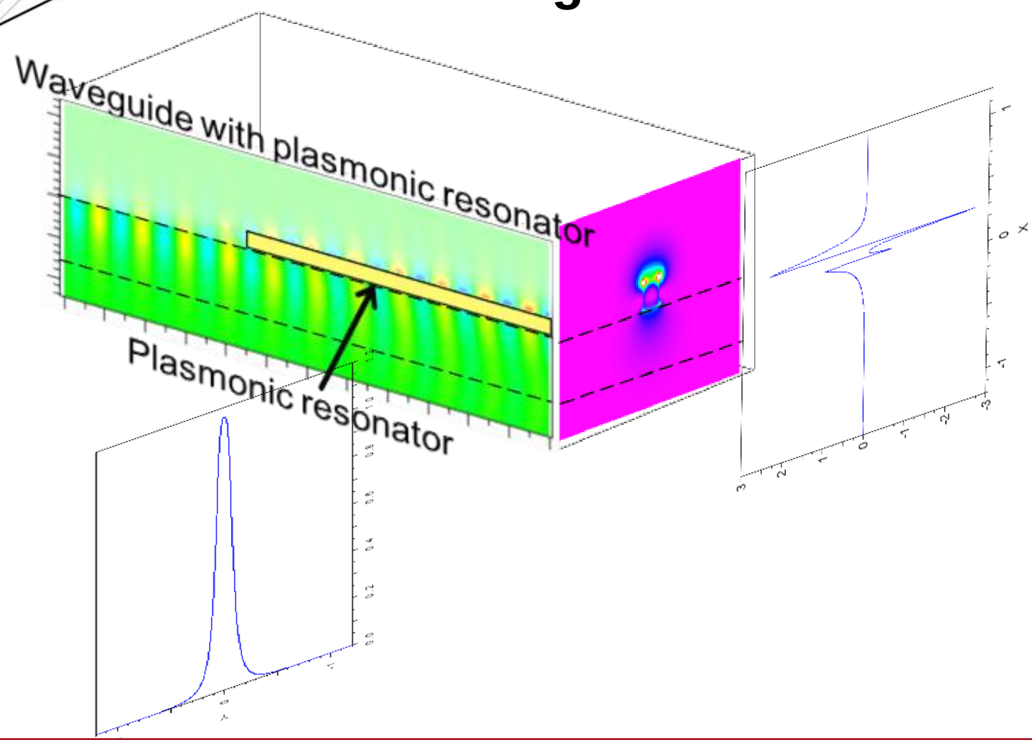
Output analogous to PCR and gel electrophoresis

Single Molecule → no PCR

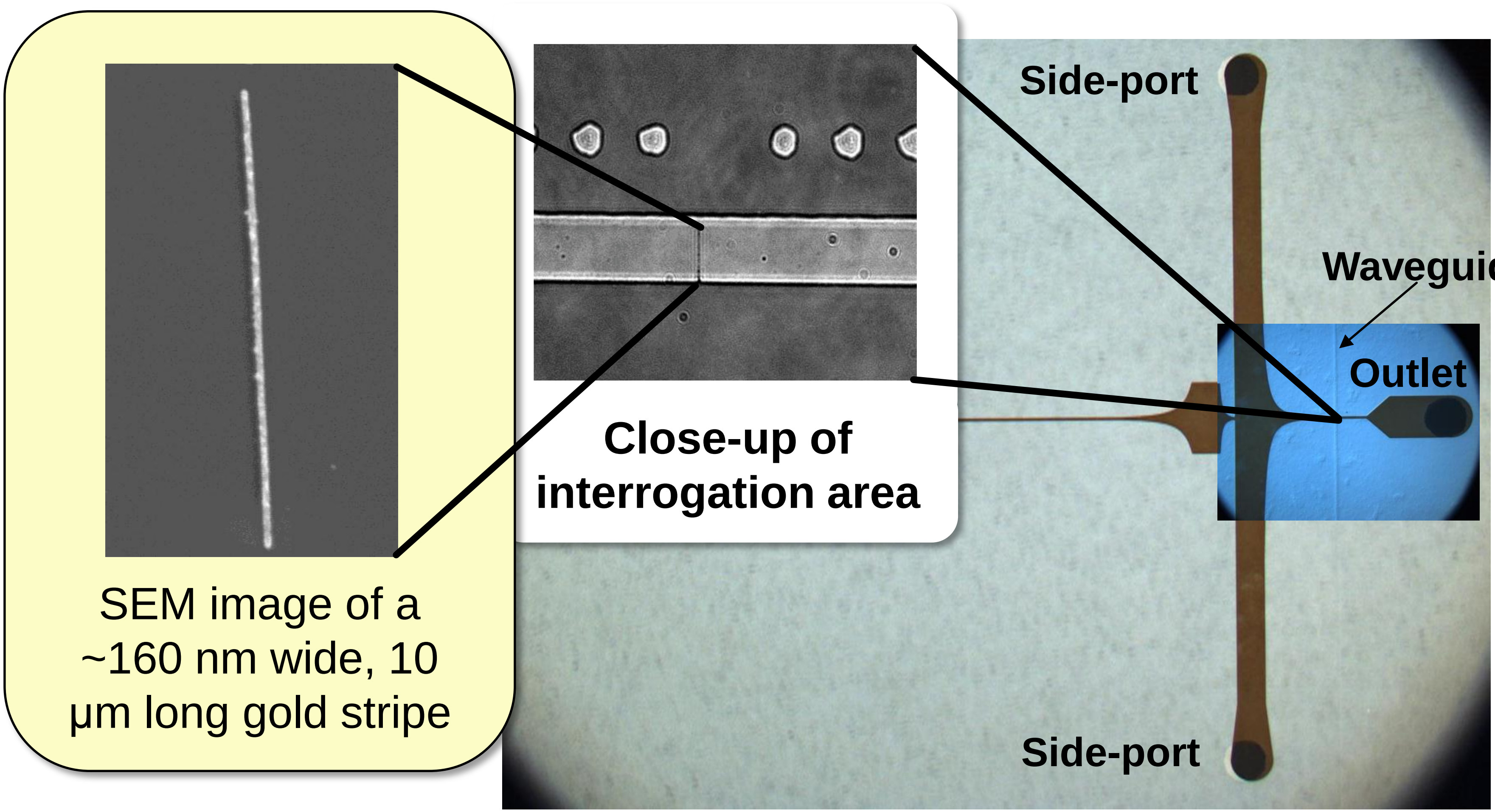


Only want excitation here, no radiation otherwise…

Plasmonic antenna confines light to << λ



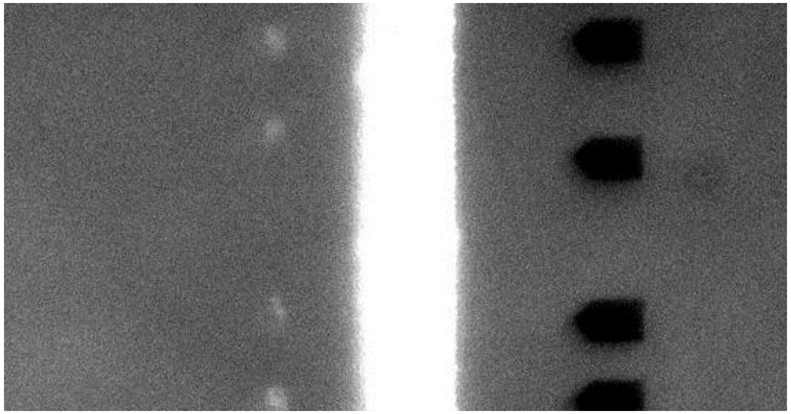
Fabrication



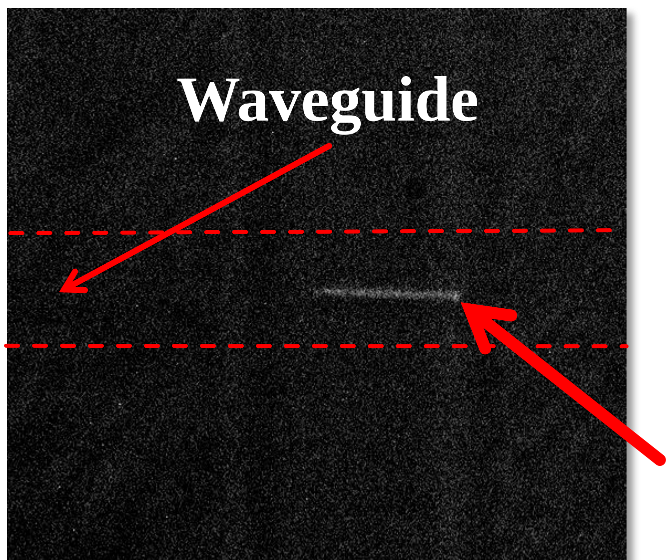
Close-up of interrogation area

SEM image of a ~160 nm wide, 10 μm long gold stripe

Testing



Channel filled with dye solution
- Arc lamp illumination



Channel filled with dye solution
- Laser input

Plasmonic resonance exciting fluorophores

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Principle of Nanohole Array Biosensing System

Extraordinary Optical Transmission (EOT)

EOT is induced when satisfying:

$$(\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2})^{\frac{1}{2}} - \sin\theta = \frac{\nu\lambda}{a}$$

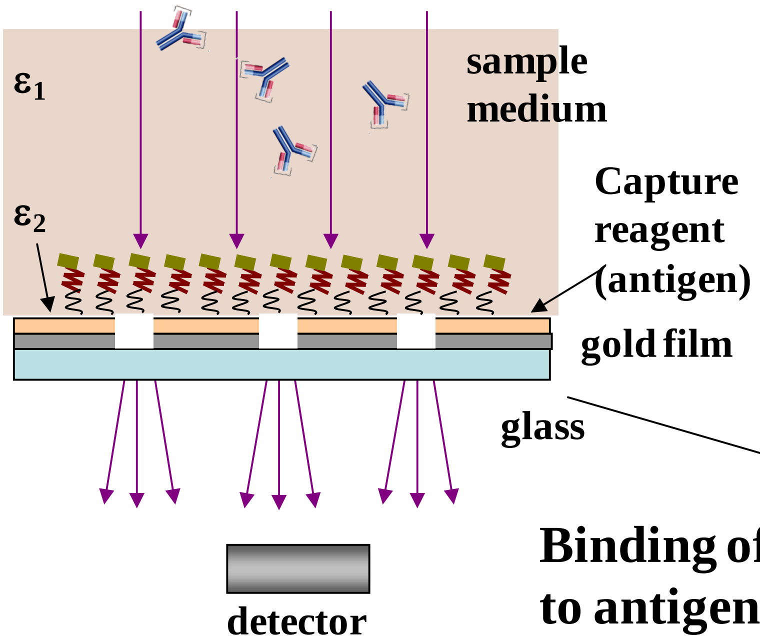
Δ in ε_1:

(1) Temperature

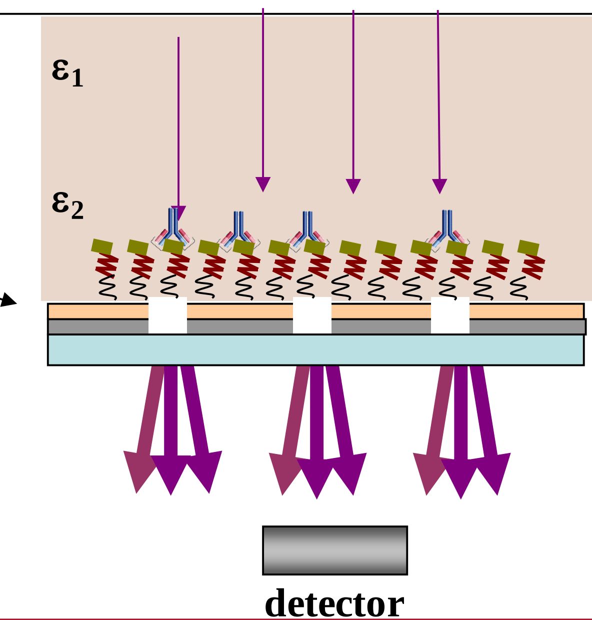
(2) Changes in the bulk medium

Δ in ε_2:

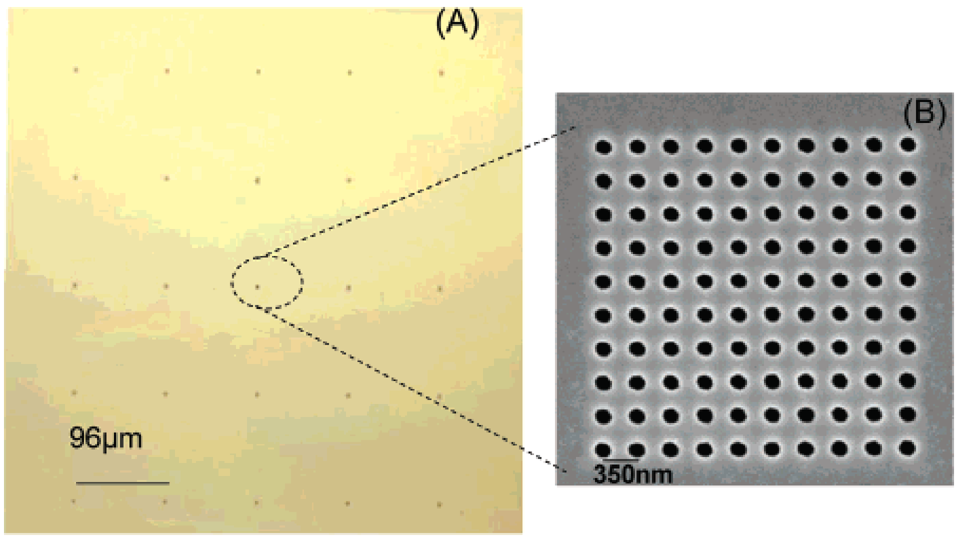
Binding or dissociation events of targets to immobilized capture agents

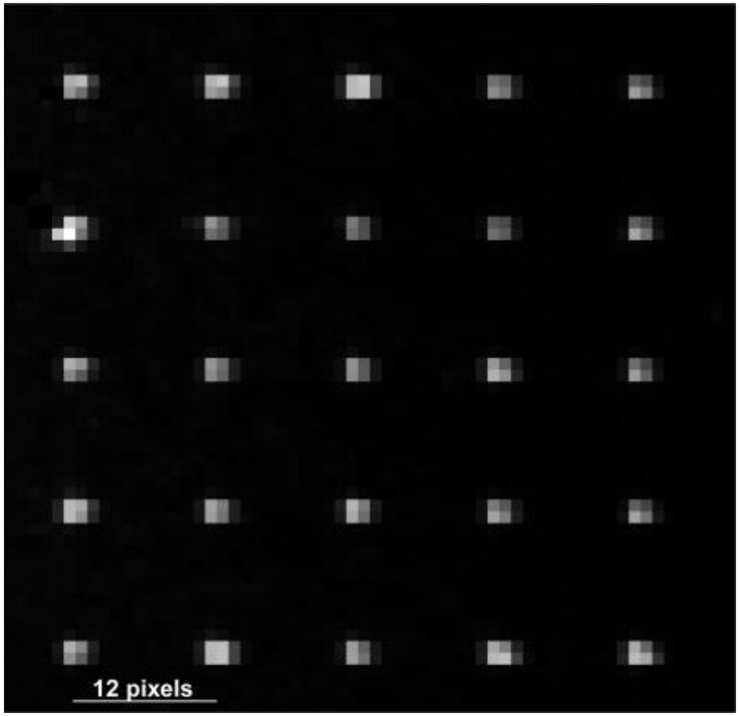


Binding of antibody to antigen induces $\Delta\varepsilon_2$, therefore ΔEOT



Possibly next generation of SPR





Potential Applications:

Binding Assays:

- **Multiplex detection of cancer biomarkers**
- **Protein array**

Calorimetry

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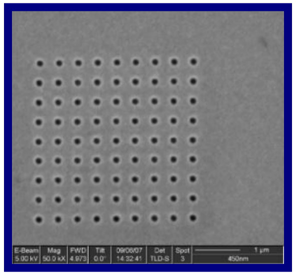
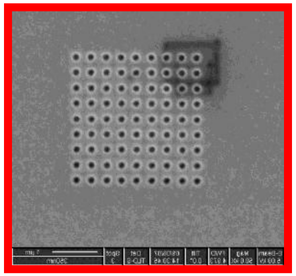
Multiplexed sensing with nanohole references

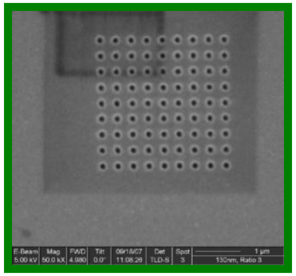
Sensor performance can be tailored



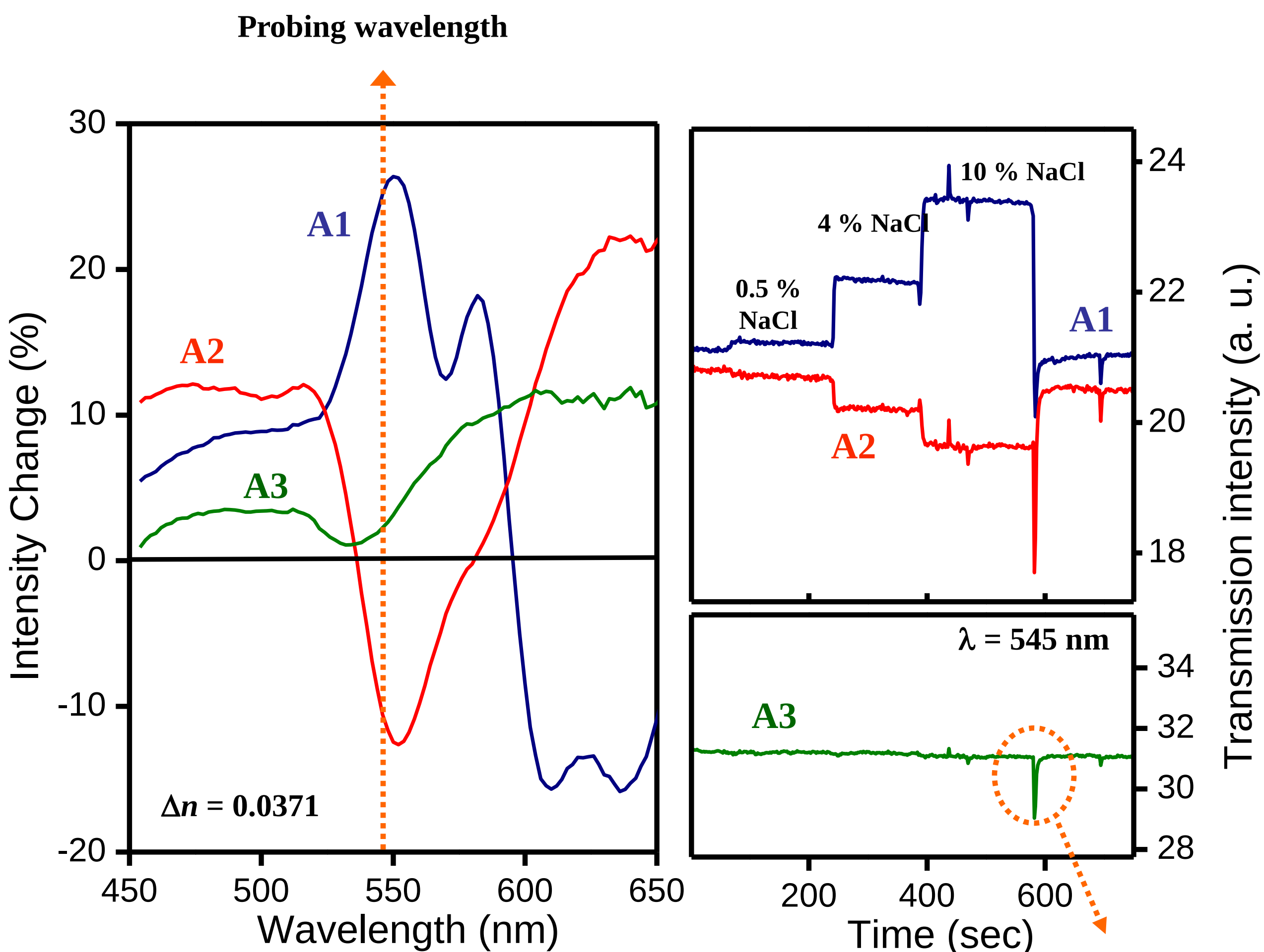
A1



A2

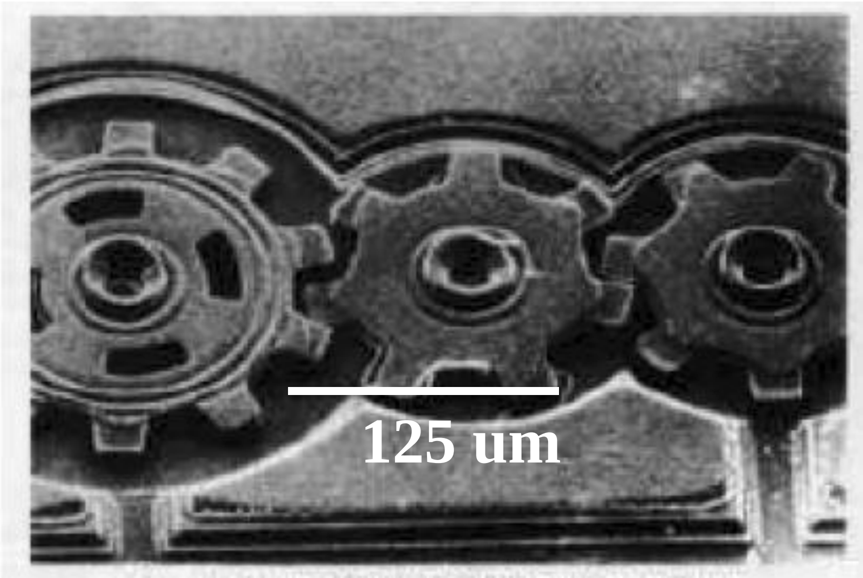


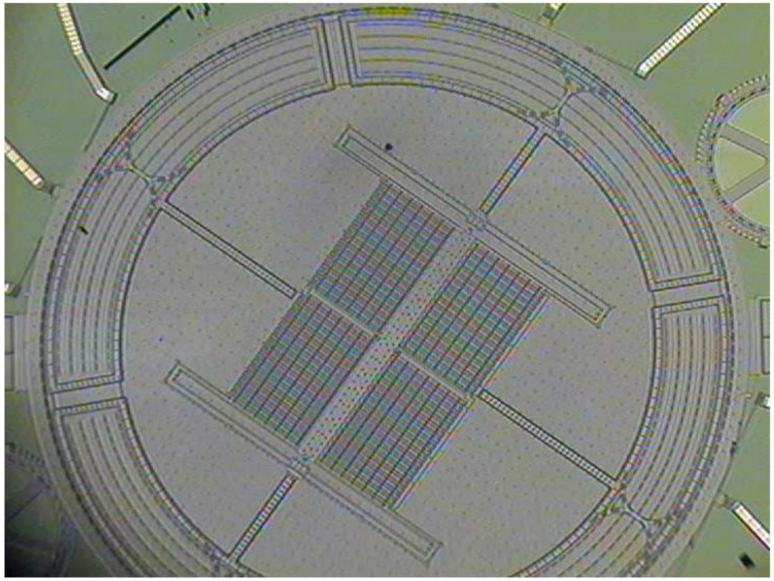
A3



MWNT Integration with MEMS

Micro & Nano Bearings





1988, Bell Labs **~2006, Sandia**

Other approaches: air bearing (MIT), ball bearings (Maryland)…

Rotational microdevices still only in limited applications (*e.g.* Sandia safe and arm)

WHY? ***Reliability, lifetime, complexity, speed, wobble***

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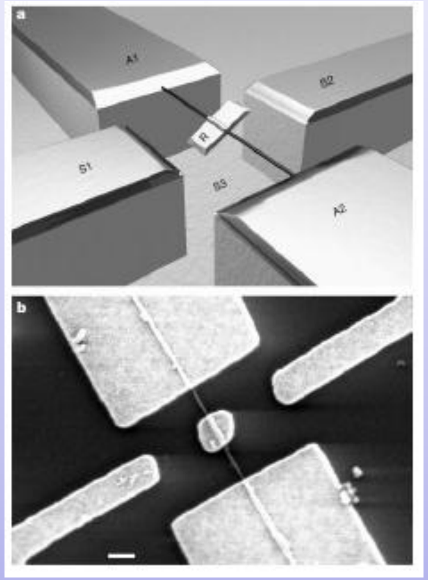
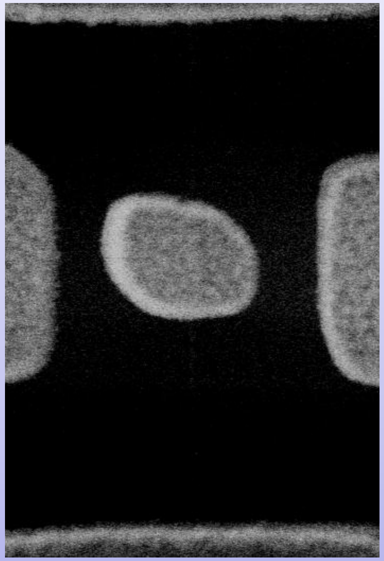
Inspiration: Previous Rotating CNT Bearing Devices





1. A.M. Fennimore *et. al*, Nature 424, 408 (2003)

3. John Cumings and A. Zettl, *Science* 289, 602 (2000).

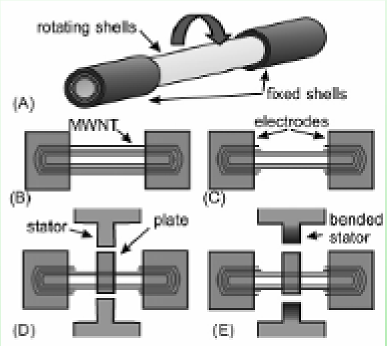
A. Zettl, et al., U.C. Berkeley. Retrieved from: http://www.physics.berkeley.edu/research/zettl/projects/Rotorpics.html

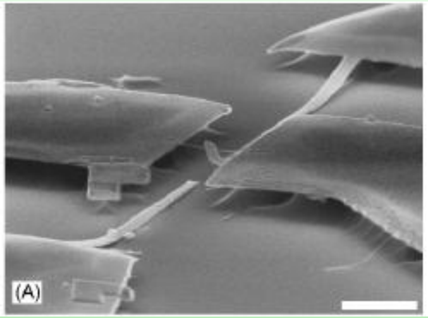
Two groups have made "see-saw" like flipper devices

(Zettl @ Berkeley, Bourlon @ École Normale Supérieure)

Accomplishments:

- Demonstrated CNT rotary bearings
- Demonstrated Electrostatic Motor
- Demonstrated long term, reliable operation
- Noted lack of wear
- One rotary static friction measurement





2. Bertrand Bourlon *et. al*, Nano Letters 4, 709 (2004)

Areas for Improvement:

Used Horizontal Tube → no axisymmetry possible

Axisymmetry would:
- improve rotor balance
- increase speed capability
- enable superior electrostatics
- enable more complex geometries

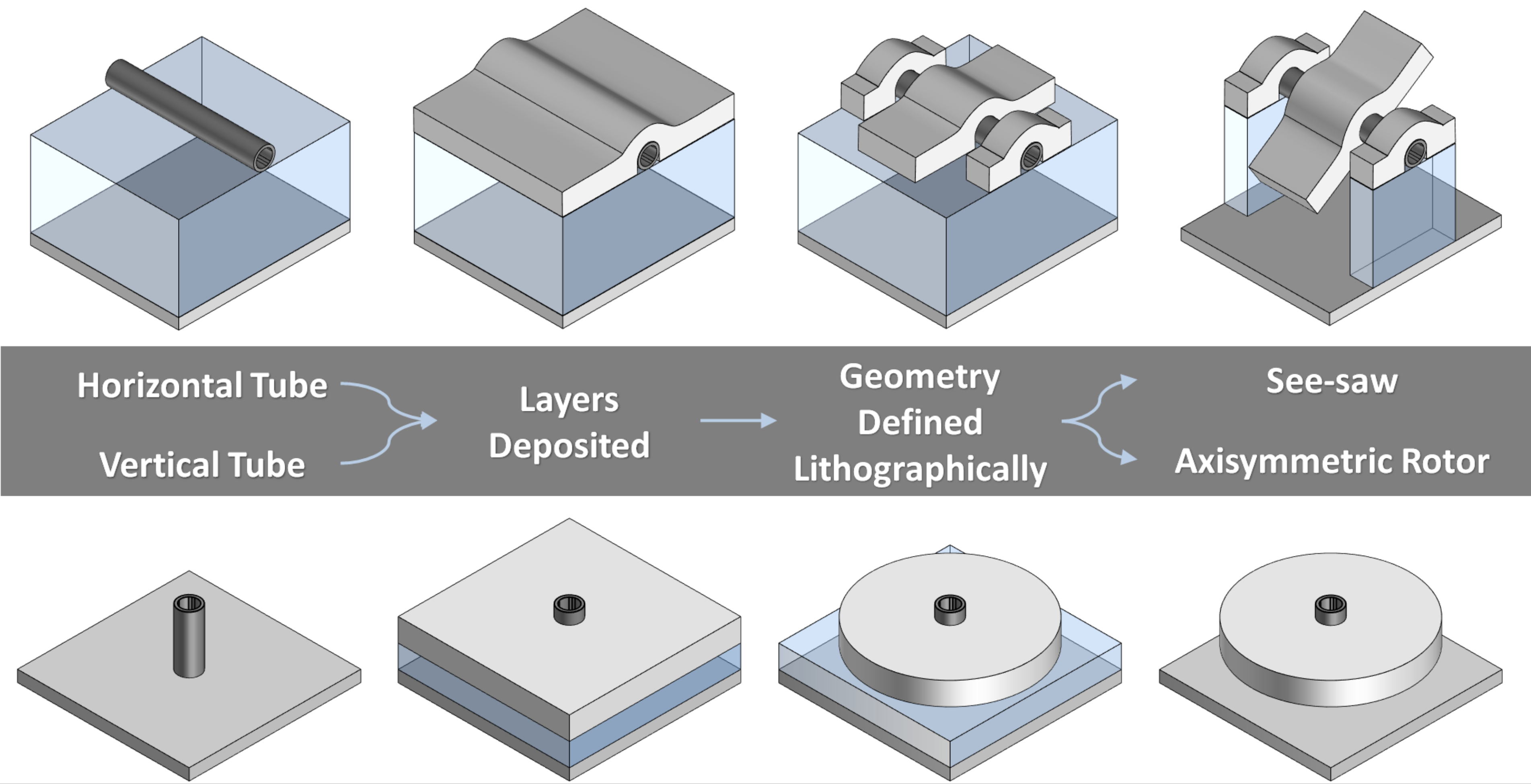
Tubes randomly distributed → no batch fabrication

No dynamic friction measurements

Draper Approach – Vertical Tube Orientation

Enables: axisymmetric design

→**superior rotor balancing, electrodes, turbine blades, etc.**



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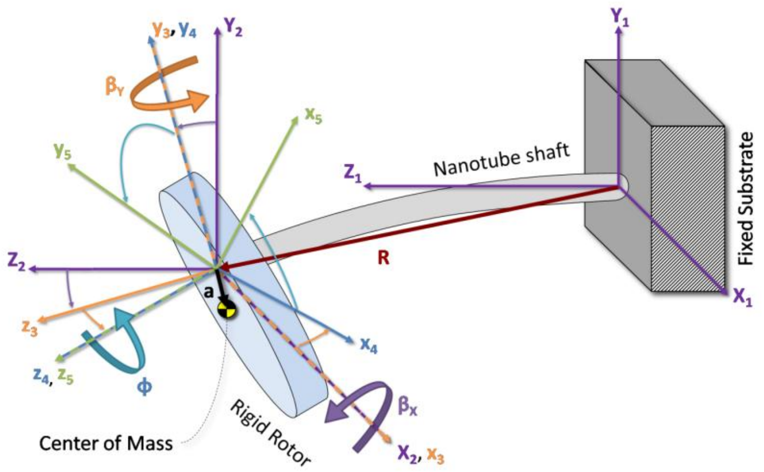
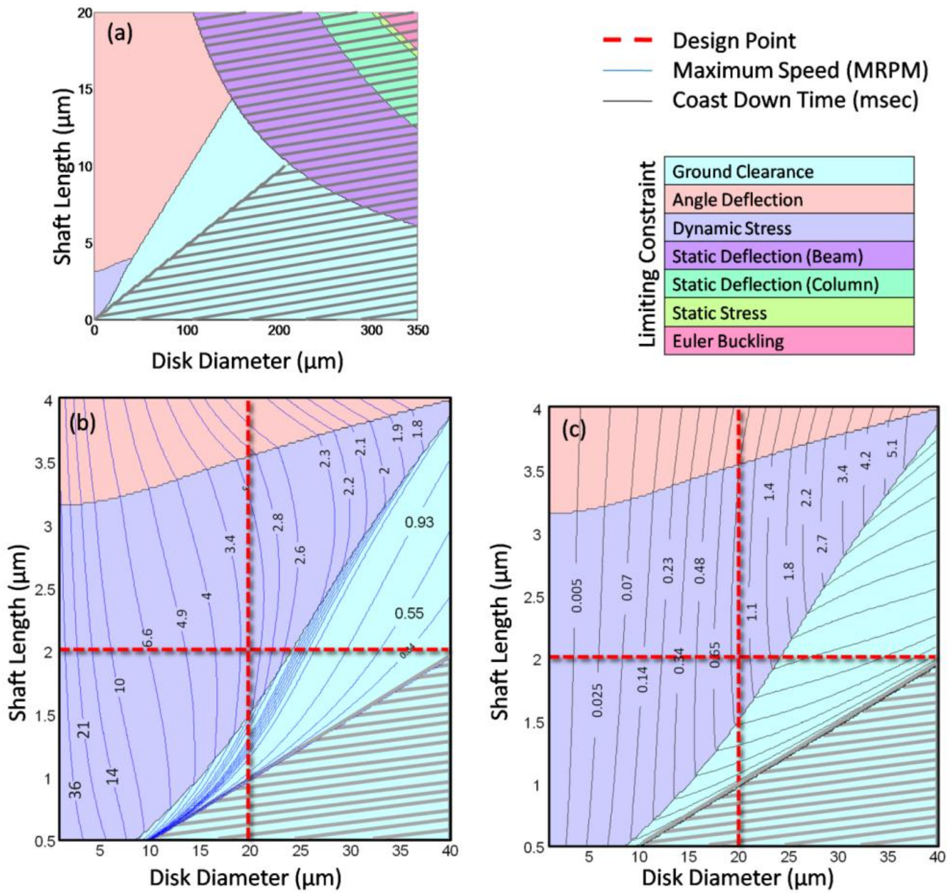
Device Rotordynamic Model

Stodola Rotor – well established dynamics
- **5 degrees of freedom**
- **Rigid thin disk, Euler simple beam shaft**

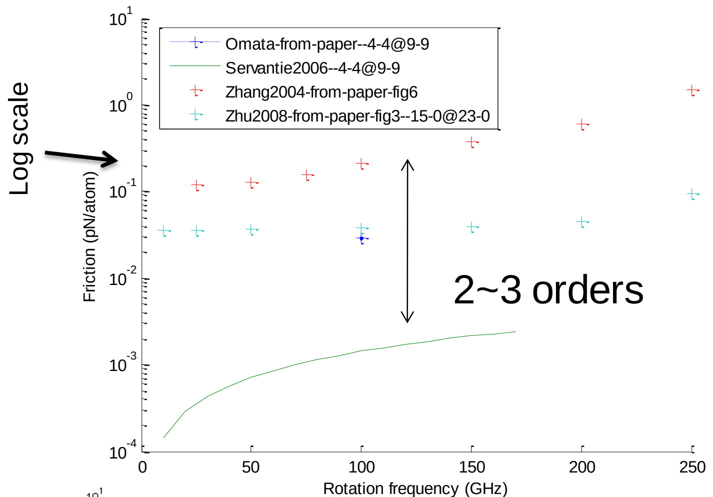
Predicts:
- **Natural & critical speeds,**
- **Angular and lateral displacements induced by imbalance**
- **Beam stresses**

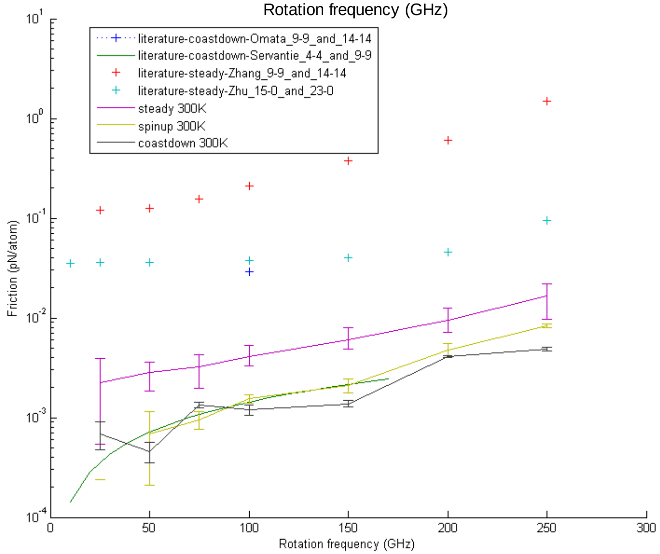




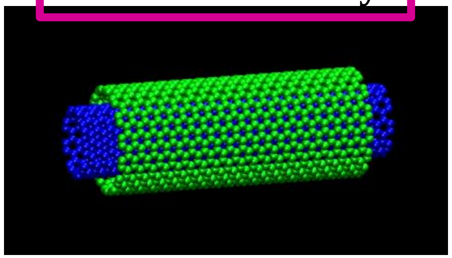
Molecular Dynamics Simulations

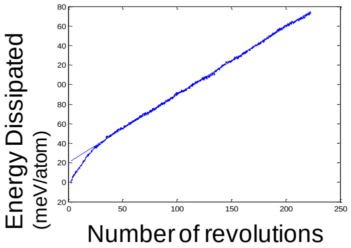
Simulation literature (without suspect papers) gives about 2-3 orders variation in MWNT friction



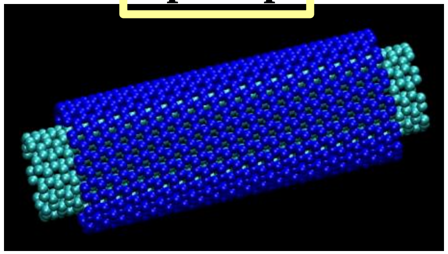


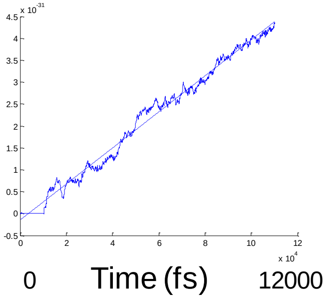
Constant Velocity



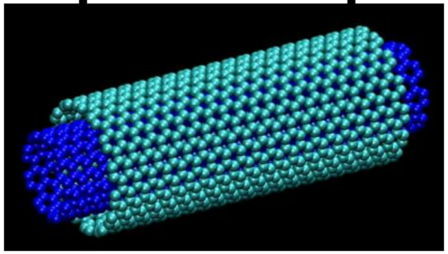


Spin-up

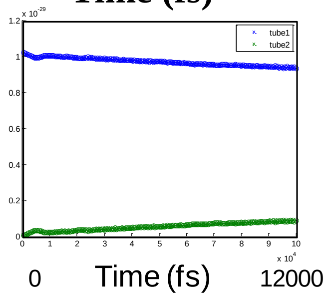




Coast-down



Time (fs)



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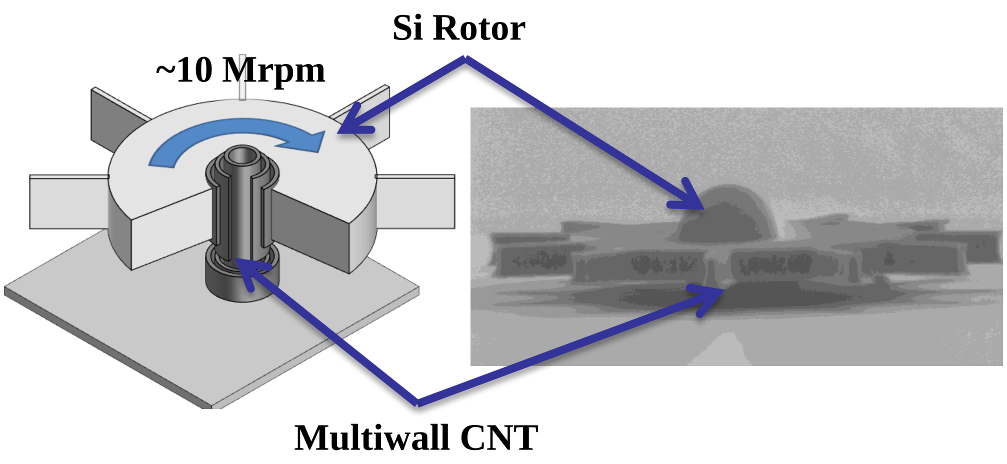
CNT/MEMS Process Compatibility

	Process	Com-patible	SEM	TEM	Notes	Other Refs	Process Parameters
Deposition	PECVD oxide	yes	x	x	Few or no defects introduced. Conformal, uniform coating. 5-10 nm layer close to tube may have altered composition - not suceptible to HF etch.	2,3	22 sccm SiH_4, 750 sccm N_2O, 430 sccm N_2, 1800 mTorr, 20W, 380° C, 30 sec
Deposition	PECVD nitride	yes	x	x	Few or no defects are introduced by PECVD. Coating is conformal, uniform.	4,5	20 sccm SiH_4, 20 sccm NH_3, 1000 sccm N_2, 650 mTorr, 20 W (7 sec @ kHz, 14 sec @ MHz cycles), 380° C, 2 min
Deposition	LPCVD poly-silicon	yes		x	No defects are introduced by LPCVD. Coating is not uniform (for thin coating); nucleates into poly-crystals.		80 sccm SiH_4, 150 mTorr, 585° C, 5 min
Deposition	PECVD amorph-Si	ok		x	Some defects are introduced by PECVD. Coating is conformal, uniform.	6	50 sccm SiH_4, 1950 mTorr, 9W, 380° C, 2 min
Etch – Wet	piranha	yes	x		Very little or no bulk damage to poorly graphitized tubes.		3 H_2SO_4: 1 H_2O_2 (30%), 30 min, room temperature
Etch – Wet	RCA SC1	ok	x	x	Did not cause much bulk damage. 1-2 outer layers may suffer slight damage. Poorly graphitized tubes showed little or no bulk damage.		5 H_2O: 1 NH_4OH: 1 H_2O_2 (30%), 30 min, room temperature
Etch – Wet	KOH	ok	x	x	Slowly introduces substantial defects at outer walls, but few defects deep within the tube. Poorly graphitized tubes showed small bulk etching.	7,8,9	45% KOH, 80° C, 30 min
Etch – Wet	dilute aqua regia	ok	x		Very little or no bulk damage to poorly graphitized tubes. Aqua regia appears to have attacked the catalyst.	10	2 H_2O : 1 HNO_3 (50-70%): 3 HCl (35%), 30 min, room temperature
Etch – Wet	isopropanol	yes	x	x	Isopropanol was used for all wet etch runs, which were dried via a critical point dryer. Some of these were compatible, so Isopropanol must also be completely compatible.		30 min (required for critical point drying)
Etch – Wet	acetone	yes	x		Very little or no bulk damage to poorly graphitized tubes.	11,12	12 hours, room temperature
Etch – Wet	dilute nitric acid	ok	x		Very little or no bulk damage to poorly graphitized tubes. May attack catalyst.	13,14	4 H_2O: 1 HNO_3 (50-70%), 30 min, room temperature
Etch – Wet	liquid buffered HF	yes	x	x	BHF does not cause bulk damage to even poorly graphitized tubes. Strips oxide from tube, except for thin layer.	15-17	35% NH_4F, 6.25% HF, 58.75% H_2O, 30 min, room temperature
Etch – Dry	vapor HF	yes	x		Very little or no bulk damage to poorly graphitized tubes.		40° C, over dish of 49% HF, 30 min
Etch – Dry	XeF_2	yes		x	XeF_2 causes no damage at all to highly graphitized nanotubes, and little or no visible damage to CVD tubes. It may cause catalyst swelling, or removal of some outer layers of amorphous carbon.		25 cycles of 1 min exposure to XeF_2 gas
Etch – Dry	SF_6 + O_2 RIE (cryo)	ok	x		May strip some outer layers of (probably amorphous) material from poorly graphitized tubes, yielding "match-sticks" with catalyst heads.		50 sccm SF_6, 10 sccm O_2, 60 mTorr, 100W, 30 min, -25° C
Etch – Dry	Ar RIE	no	x		Severe damage or polymerization after long etch. Sharpens tube, causes significant bending.	18	30 sccm Ar, 60 mTorr, 100W, 30 min, room temperature
Etch – Dry	SF_6 RIE	no	x		Severe damage or polymerization after long etch. Sharpens tube, causes significant bending.		60 sccm SF_6, 60 mTorr, 100W, 30 min, room temperature
Etch – Dry	SF_6 + O_2 RIE	no	x		Severe damage or polymerization after long etch. Sharpens tube, causes significant bending.		60 sccm SF_6, 10 sccm O_2, 60 mTorr, 100W, 30 min, room temperature
Etch – Dry	CF_4 RIE	no	x		Severe damage or polymerization after long etch. Sharpens tube, causes significant bending.		25 sccm CF_4, 60 mTorr, 100W, 30 min, room temperture
Etch – Dry	CF_4 + O_2 RIE	no	x		Causes etching at the tip, possibly just due to sputtering (as it is uniform across etch chemistries). Sharpens tube.	5	25 sccm CF_4, 5 sccm O_2, 60 mTorr, 100W, 30 min, room temperature
Etch – Dry	DRIE	yes	x		Non-aggressive recipe; little or no bulk damage to poorly graphitized tubes.		Etch cycle: (130 sccm SF_6, 13 sccm O_2, 20 mTorr, 150W ICP, 22W platen, 8 sec) Passivation cycle: (100 sccm C_4F_8, 20 mTorr, 600W ICP, 22W platen, 5 sec) Overall: (16 cycles, 2:48 minutes)
Etch – Dry	CHF_3 + CF_4 RIE	no	x		Causes etching at the tip, possibly just due to sputtering (as it is uniform across etch chemistries). Sharpens tube, causes significant bending.		14.6 sccm CHF_3, 1.4 sscm CF_4, 20 mTorr, 200W, 30 min, room temperature
Etch – Dry	O_2 plasma RIE					19	30 sccm O_2, 60 mTorr, 100W, 30 min, room temperature
Etch – Dry	O_2 plasma ash	no	x	x	Oxygen plasma attacks amorphous carbon strongly, and nanotube walls slowly. Poorly graphitized tubes are strongly damaged. Well graphitized tubes are undamaged.	17	40 sccm O_2, 200 mTorr, 55W, 30 min, room temperature

Status

Device Fabrication Demonstrated

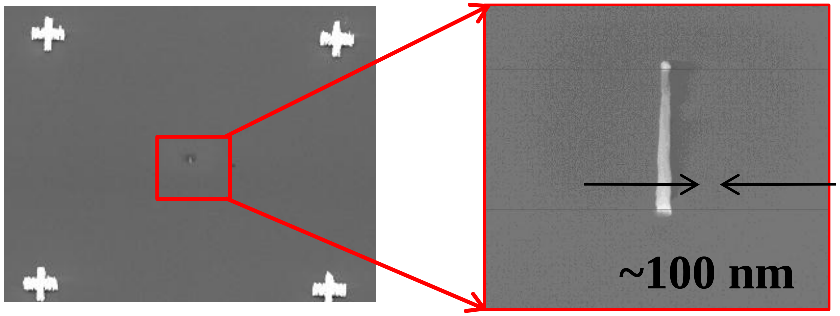


CVD nanotube quality inadequate for rotation (also true for COTS nanotubes)

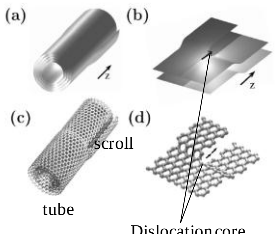
- **Built chamber and optimizing arc-deposition process**
- **Investigating pick-and-place in FIB/nanomanupilator**
- **Possibly electrophoretic placement**

MWNTs

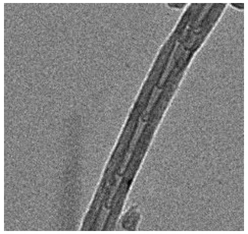
(PE)CVD-grown



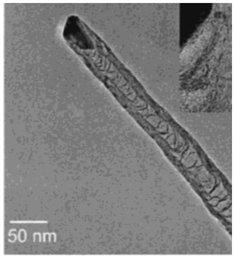
Issue: Defects



Tube wall defects

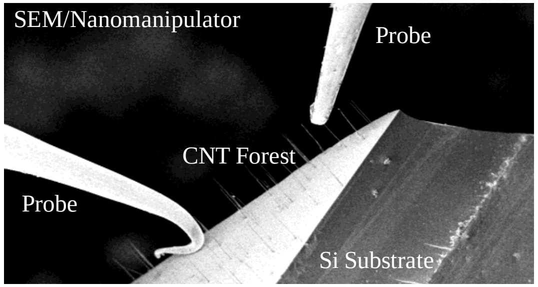


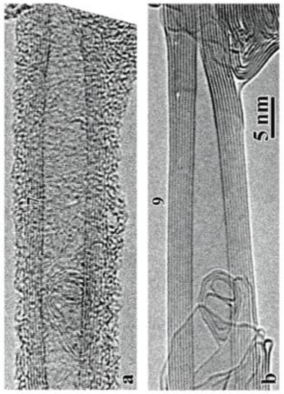
Bamboo Defects



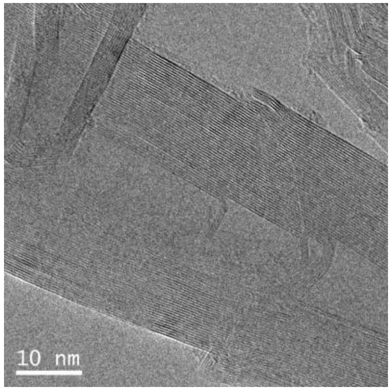
Bowing

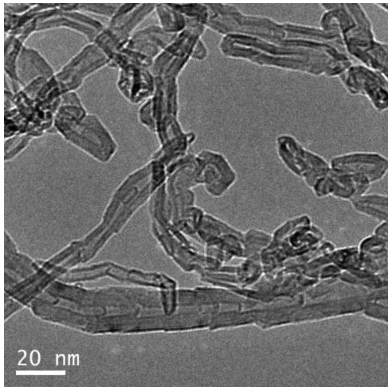
Solution: Current Annealing





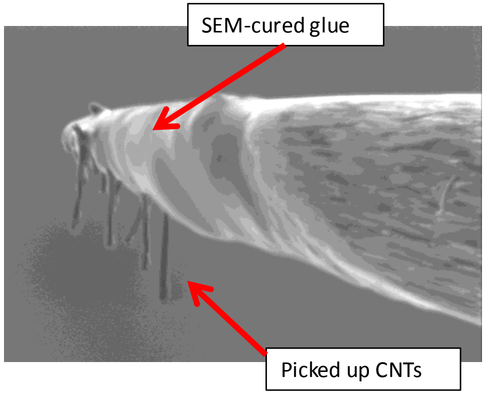
COTS Graphitized MWNTs





Locally: good crystallinity, no amorphous carbon
Larger-scale: defects (bamboo, kinks, chevrons, etc.)

Arc-Grown CNTs w/ pick-and-place



Thoughts on Challenges and Opportunities for Integrated Nanosystems

- Microfab/top-down nanofab bootstraps from the semiconductor industry
  - *Very good* at planar fabrication
- May not want nanostructures/materials to be planar for best utilization
  - MWNT Bearing offers advantages to going perpendicular to the substrate (~2.5D?)
  - Most surface plasmon structures are 2-D (maybe 2.5D)
    - 3-D could offer optical metamaterials, optical cloaking devices, etc.
  - Biology is not planar; nano-bio interface offers *huge* rewards
  - ***How to fabricate 3D nano/micro structures and interface them with macro structures***
- Best nanostructures may be produced in a messy batch process
  - *e.g.* Arc-deposited MWNTs
  - ***Techniques to precisely sort/place nanostructures/mat'ls onto/into 2D/3D structures***
- ***Multiscale/multimode simulation*** to fully understand structures and interactions
  - Spanning from molecular interactions potentially to meters
  - *e.g.* To model gecko: 8 o.o.m. in size (mechanical structures): VdW w/surface, ~100 nm spatulae, ~10100 um setae, few-mm toes, ~cm paws, ~10 cm body
- ***Fault-tolerant design*** for nano/micro/macrosystems
  - Self-assembly will have defects (thermodynamics)
  - Need electrical, mechanical designs that can deal with those defects
    - Computation, biosensor, gecko adhesive support structure, etc.

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