Materials Requirements and Measurements in Nanoscale Manufacturing and Assembly

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Our Vision

To be the the leading worldwide supplier of tools, products, and services that enable adaptable, affordable, and molecularly precise manufacturing.

Corporate Introduction

- Privately held company
- Founded in 1997
- Located in Richardson, Texas
- Detailed Five-Year
  Strategic Business and Marketing plans
- Detailed Technology Roadmap
- Aggressive IP strategy
- Extensive list of scientific and business publications

Resources

- Headcount: 52 and increasing
  - 17 Ph.D.s
  - Engineers, scientists, technical management
- 44,000 sq. ft. facility
- Class 100 clean room
- Several fully equipped laboratories
- CNC-equipped machine shop
- Equipment: SEM, TEM, AFM, SPM, UHV STM, numerous lasers, MEMS motion analyzer, electrical testing station

General Questions

- What is considered state-of-the-art, in terms of experiment/ processing/ characterization **and/or** theory/ modeling? (this may include some of your own work)
- What are the problems now under investigation?
- What barriers (scientific and/or technological) do you foresee to advances in the coming 5 to 10 years? Please include barriers that may be addressed by improvements in materials measurements.
- What are possible approaches to solution? Please include how you might envision “division of labor,” i.e. roles of industry, DOE labs, NIST, universities.

Questions for Fabrication Speakers

- How is mechanics/mechanical behavior important in terms of performance and reliability required at product level?
- How do you design-in performance and reliability, using principles of micro- and nanostructure control? Please comment on adequacy of existing lifetime or performance prediction methods.
- How does industry measure performance of both the end product and the constituent materials?
- What are the limitations/barriers of the present measures/metrology?

My Agenda

- MicroSystem Assembly
  - What Zyvex is doing with MicroAssembly
  - Metrology Requirements
  - Material Requirements

- Nanomaterials
  - Zyvex's CNT functionalization technology
  - Metrology & Analysis Requirements
  - Material Requirements

- Atomically Precise Manufacturing
  - Zyvex's Vision of APM
  - Metrology Requirements
  - Material Requirements

MicroSystem Assembly

Micro-Miniaturization

- **IC Progress**
- **Litho-Centric: Downscaling**
- **Parallel Processing**
- **Monolithic Integration**
  - Not the universal answer
  - Demands compromises
  - Logic and memory divergence
- **Assembly Manufacturing**

We are trying to do for assembly what Noyce and Kilby did for electronics.
Dramatically lower cost and provide downscaling path.

Early Technology

- **Pointed Sticks**
  — early processing
- **Stone tools**
  —monolithic integration
- **Spear with stone spearhead**
  — Heterogenious integration
  —AKA Assembly

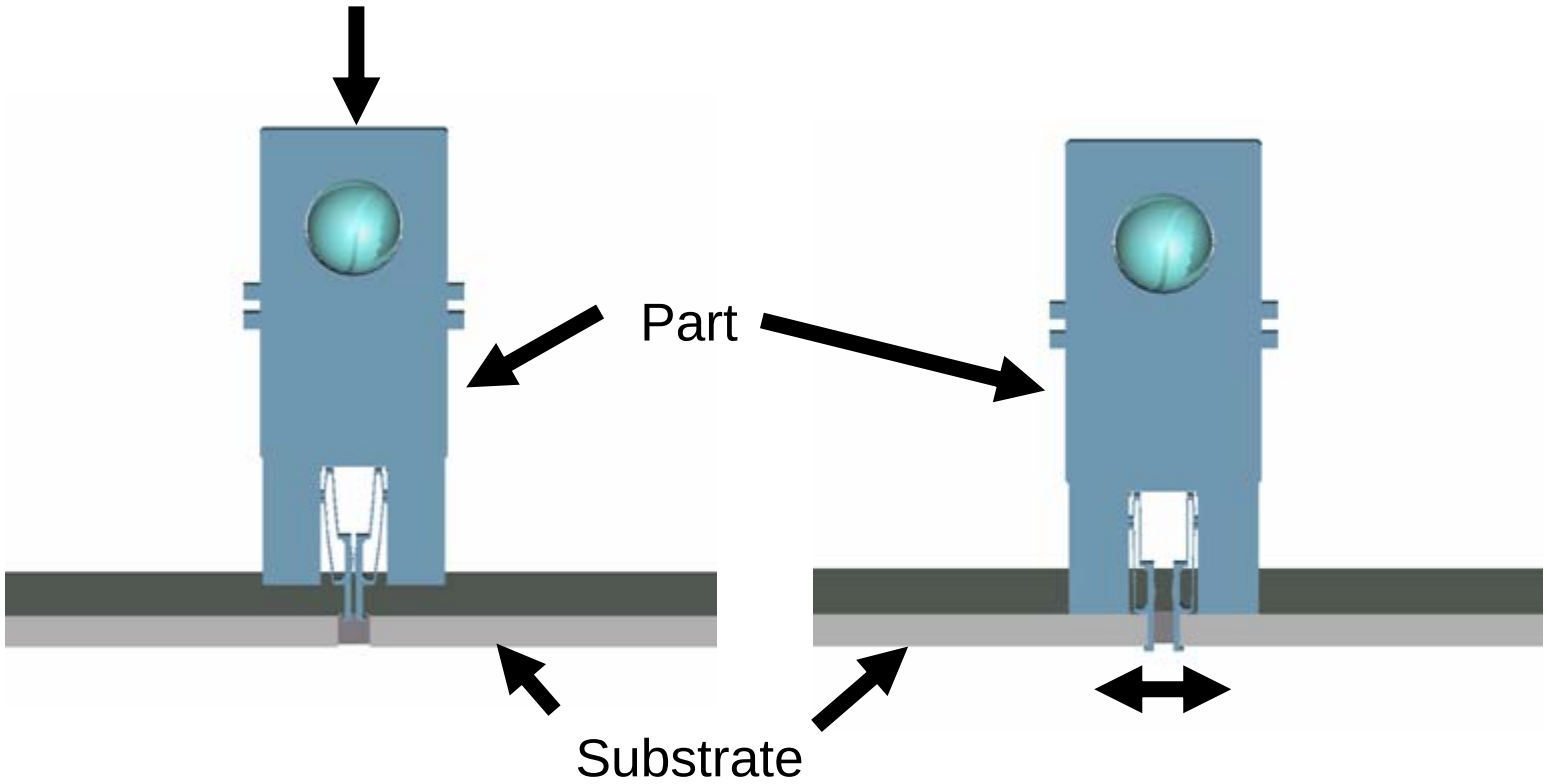
Sad Fact #1

- IC industry has < 0.1um Gates in production
- Eigler demonstrated assembly of atoms 14 years ago!
- Assembly manufacturing has no solution for parts <0.5mm.
- Humans are used to assemble parts <0.5mm.

Sad Fact #2

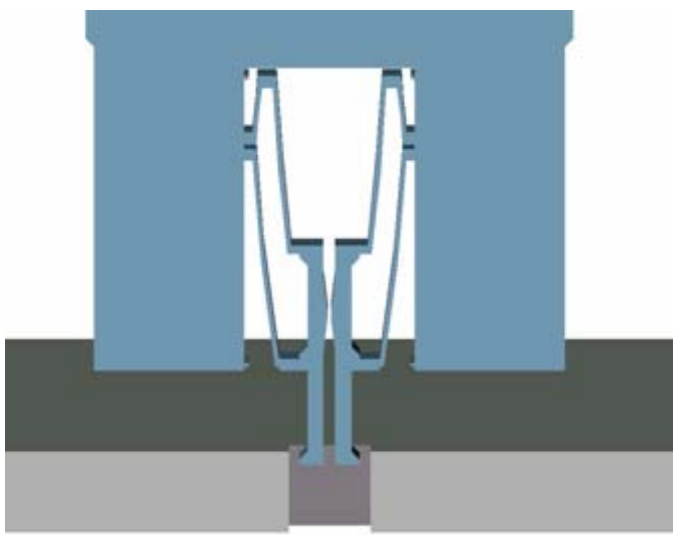
- **Virtually all assembly manufacturing is done serially.**
- **Improving COO increased principally with speed of assembly operation.**
- **Historically this makes sense.**
  —Parts comparable in size to assembly robots
- **With small systems and small parts this now becomes possible.**
- **Dramatic improvements in COO with parallelism.**

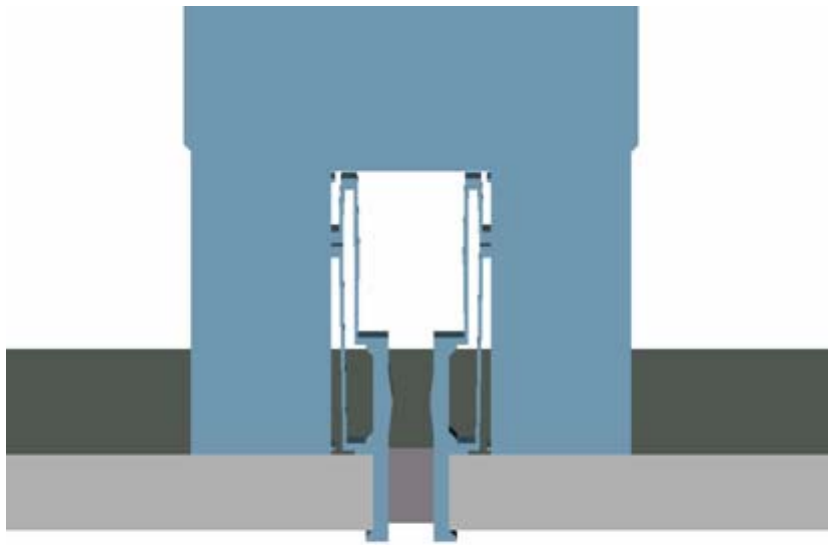
Micro Snap Connectors



Zero insertion force Si snap connectors provide robust mechanical connection.

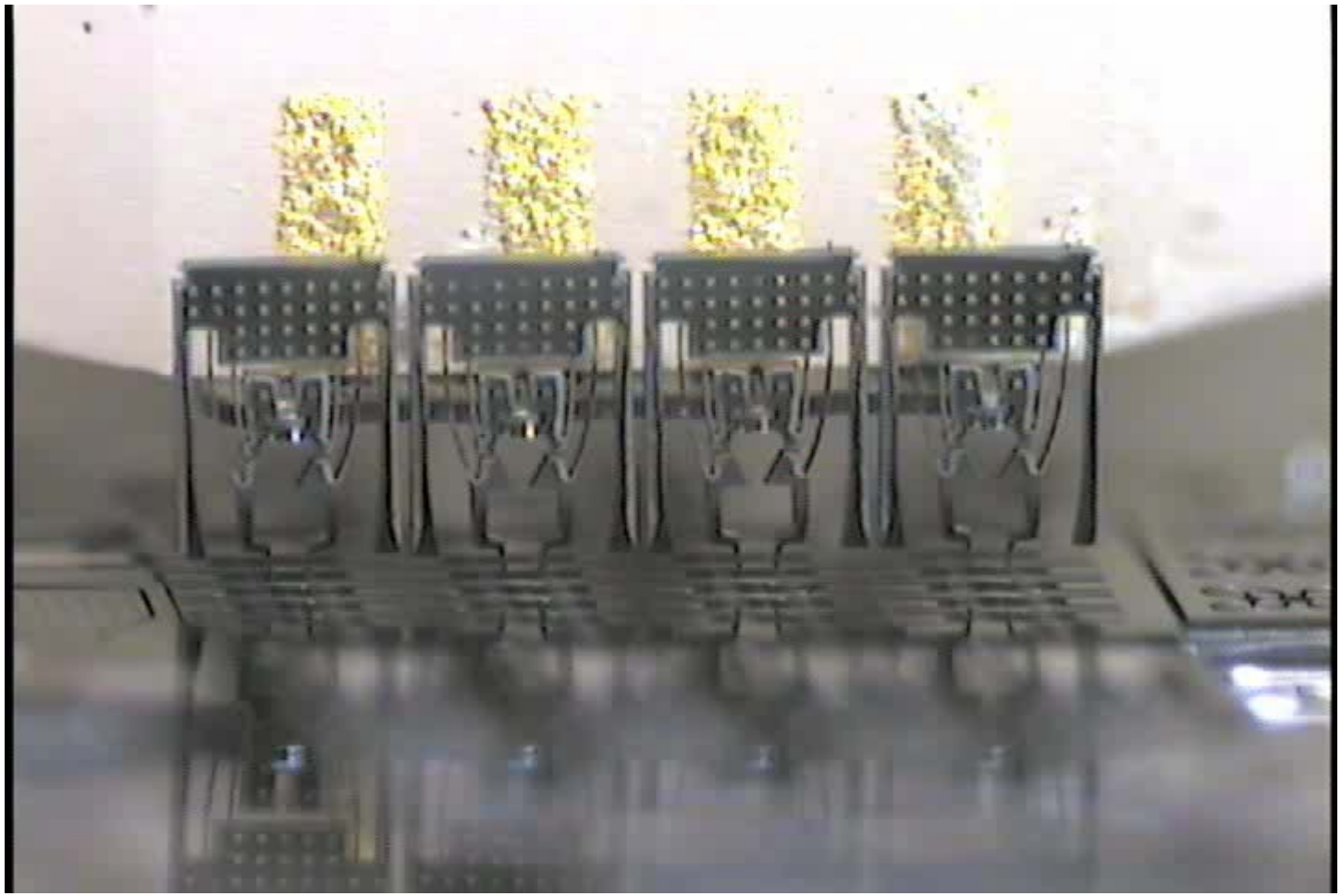
Parts Bound to Assembly



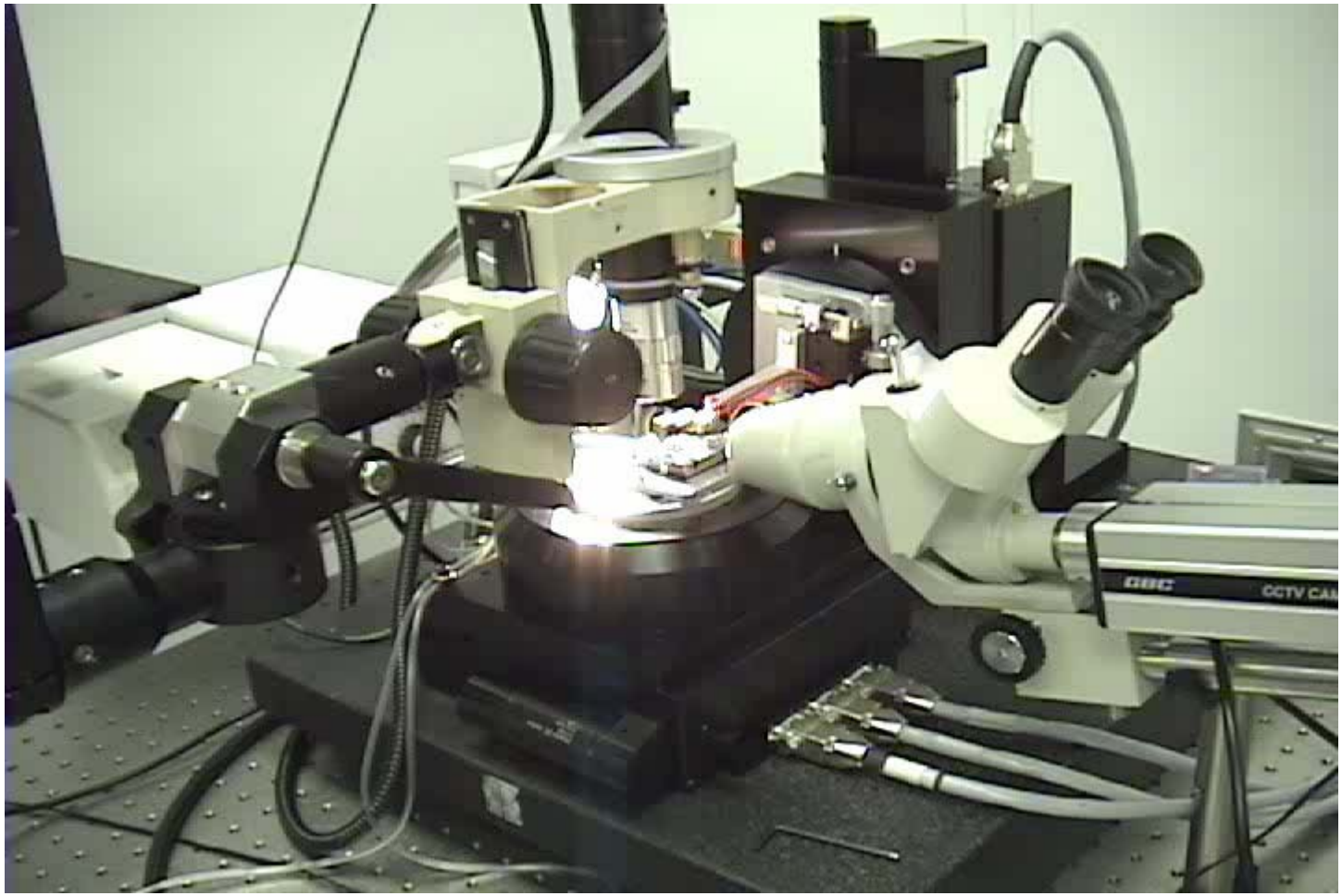


Zero insertion force Si snap connectors provide robust mechanical connection AND better placement accuracy than robot by self-centering mechanism.

Parallel Assembly of Snap Connectors

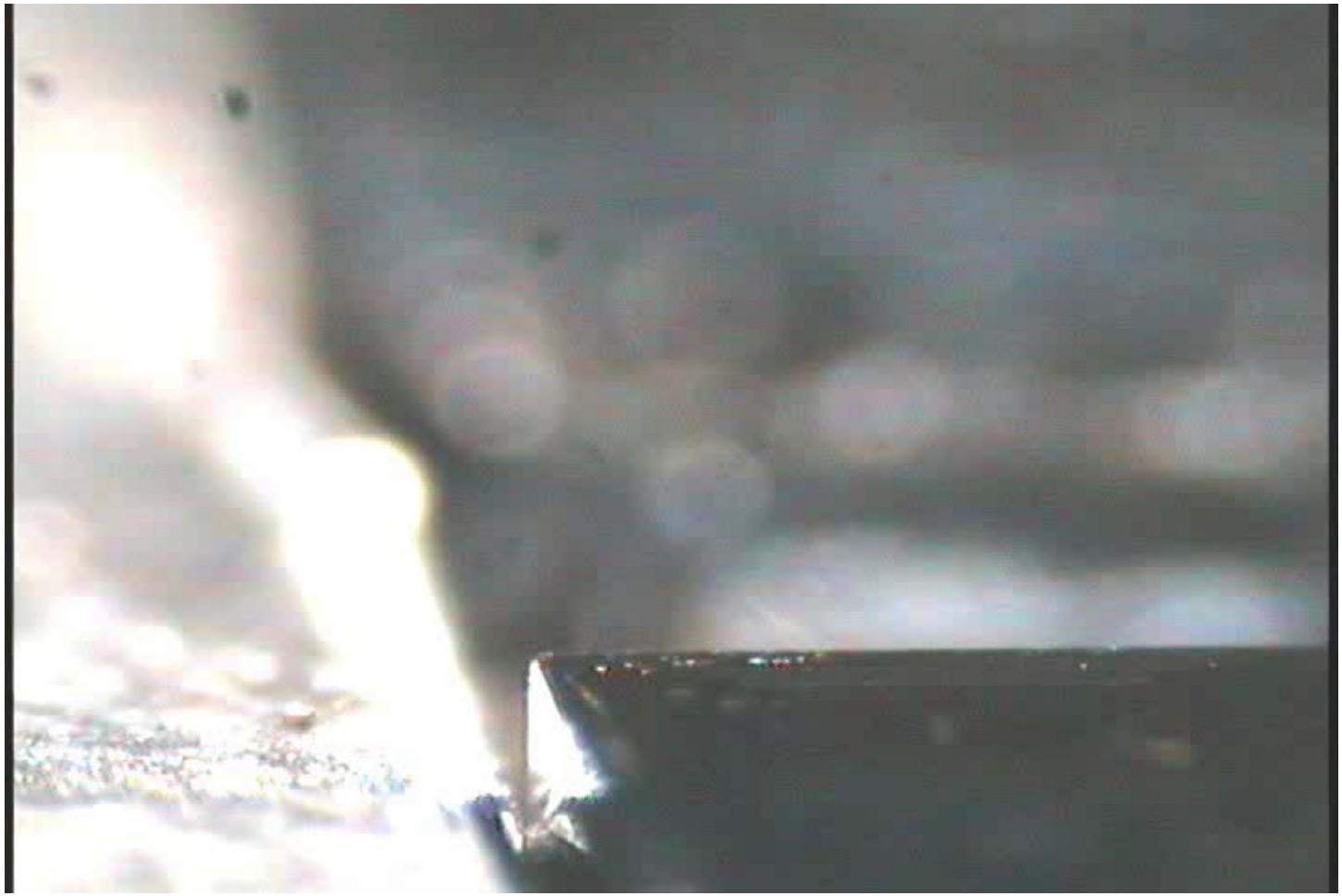


Automated Scripted Assembly of two deflector plates for a mini-SEM



Macro - View

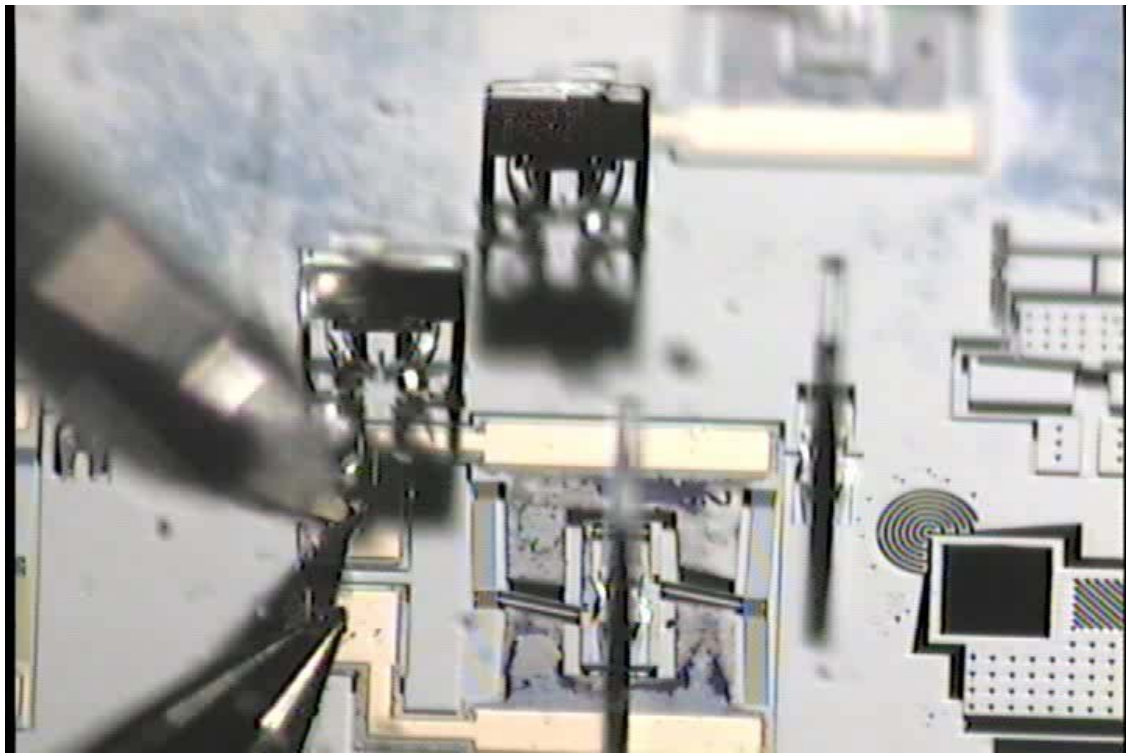
Automated Scripted Assembly of two deflector plates for a mini-SEM



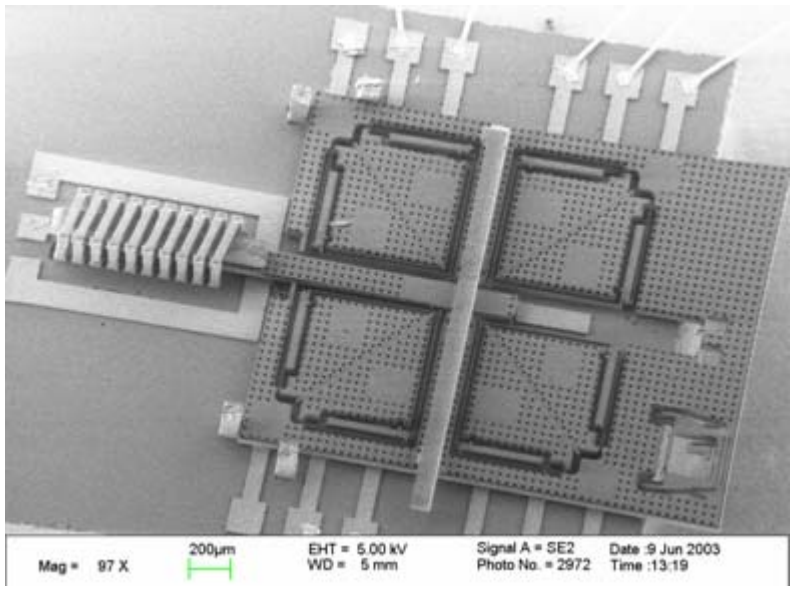
Micro – View, same assembly

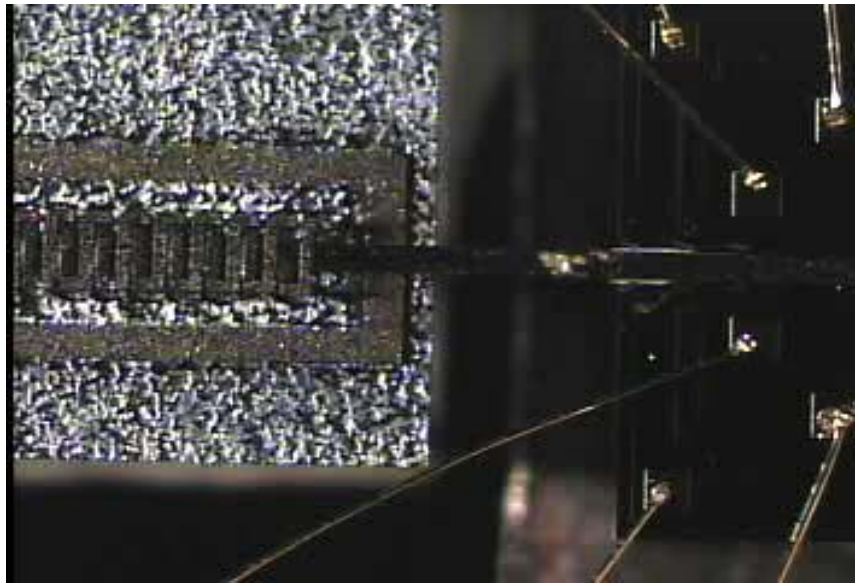
VOA Beam Steering Design

- Three stationary mirrors
- One active mirror



Variable Inductor





- Three components from three MEMS processes
  - Silicon linear micromotor
  - Copper inductor
  - Ni-Fe magnetic core

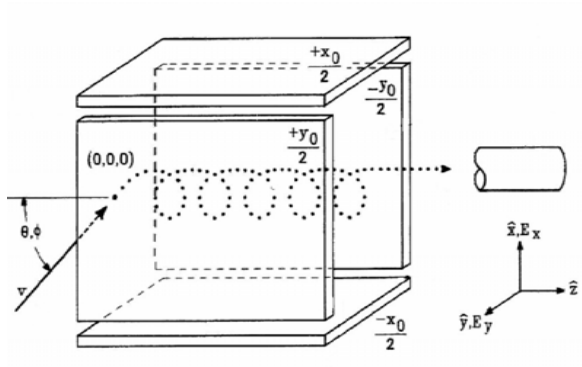
The Zyvex Approach
Microassembled mass spec.

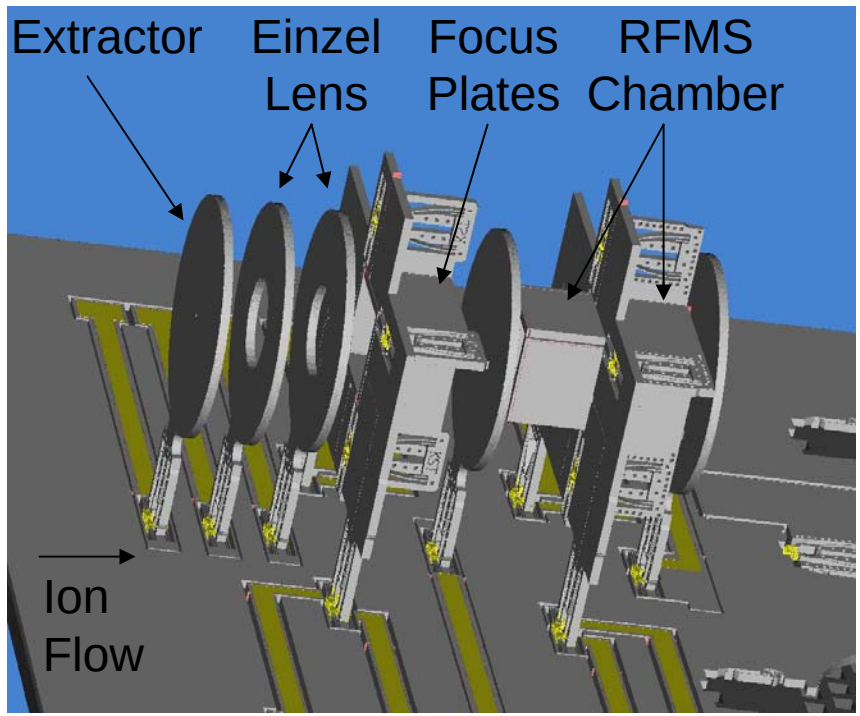
Description and Concept:

- Electrostatic plates for ion focusing
- Ion dispersion chamber consisting of microassembled RF deflection plates

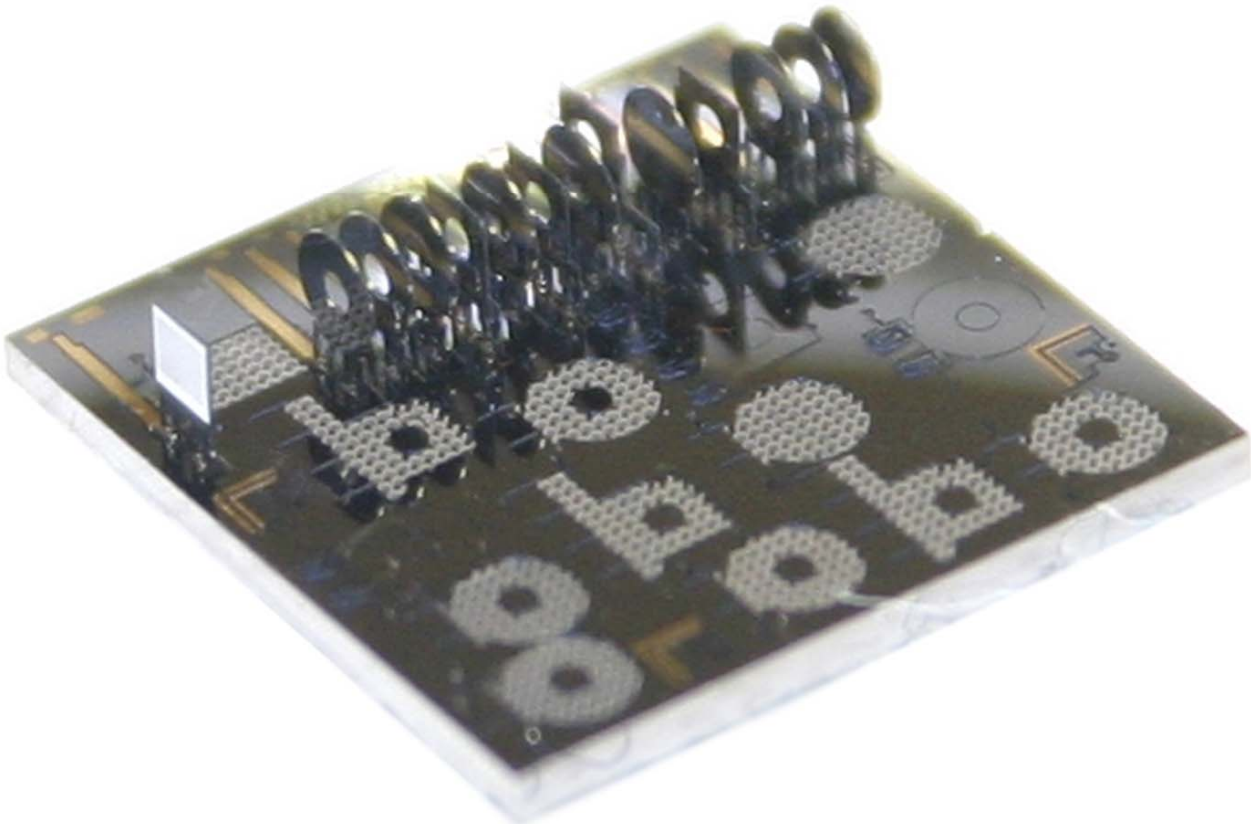
Future Work:

- Micromachined ionization
- On-chip electronics for control and detection
- Miniature vacuum components





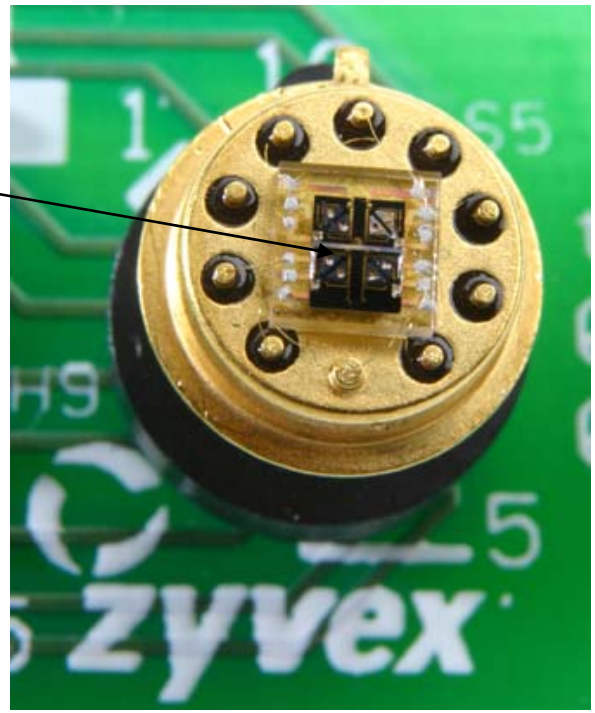
Assembled Micro-SEM Column



Assembled Linear Actuator

- Assembled linear actuator
  - Wire bonded device on TO-100 package

Micro assembled linear actuator



Metrology Requirements

- Accuracy of assembled components in microsystem
  - Large required DOF (3D structures)
  - Indirect measurements (optical systems)
  - Holographic approaches

- Dynamic measurements
  - Umech & Veeco instruments
  - Micro stress and force sensors

- Tribology of Micro structures
  - MEMS rotational and slide bearings suck

Material Requirements

- Silicon is wonderful and is fairly well understood
- Tougher materials
  - Noel McDonald is working with Ti
- Heterogeneous integration desired
  - IC processing accuracy in many new materials
  - MEMS rotational and slide bearings suck

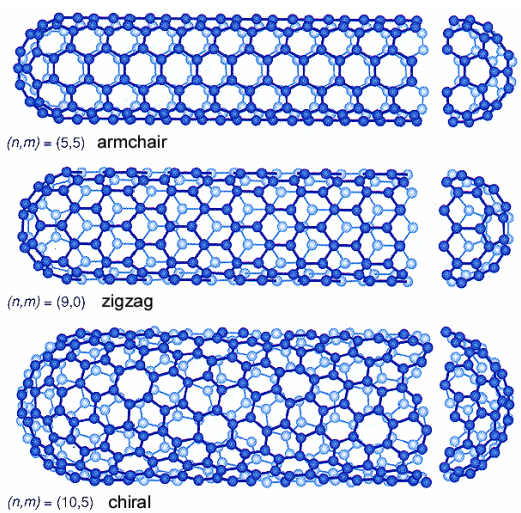
Nanomaterials

Nanomaterials - Composites

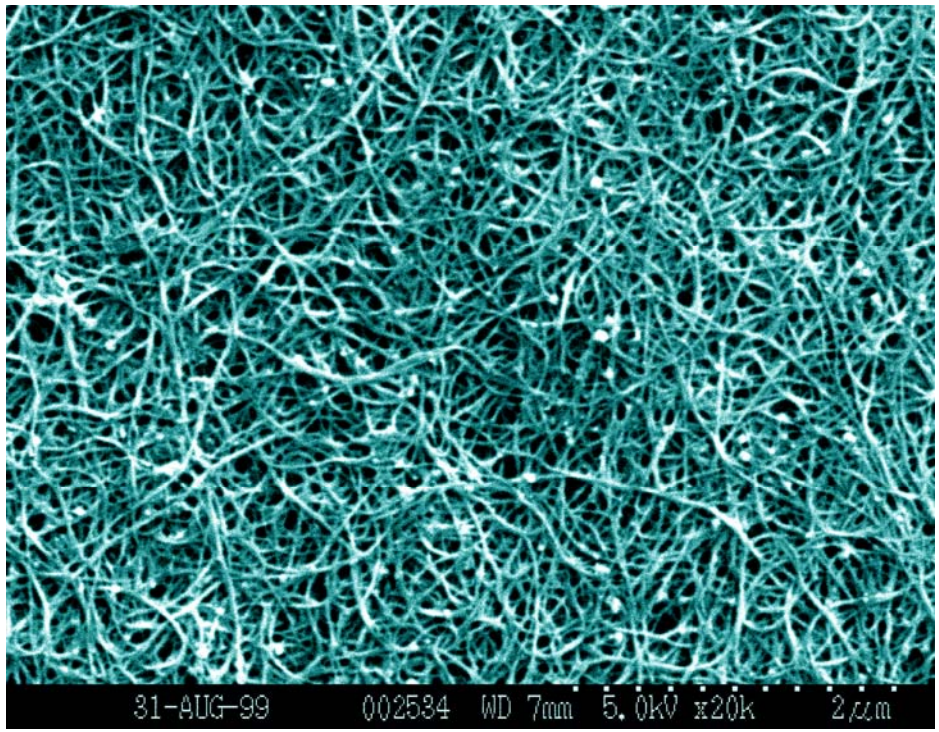
- Composite materials are everywhere.
- Synergistic combinations of dissimilar materials (heterogeneous integration) can have a big payoff.
- Performance in Composite materials have plateaued.
- Nanocomposites have gotten significant attention, but <u>the performance has yet to match the hype.</u>

Superior Properties of Carbon Nanotubes

- High Mechanical Strength
- High Electrical Conductivity
- High Thermal Conductivity
- High Chemical and Thermal Stability
- Light Weight

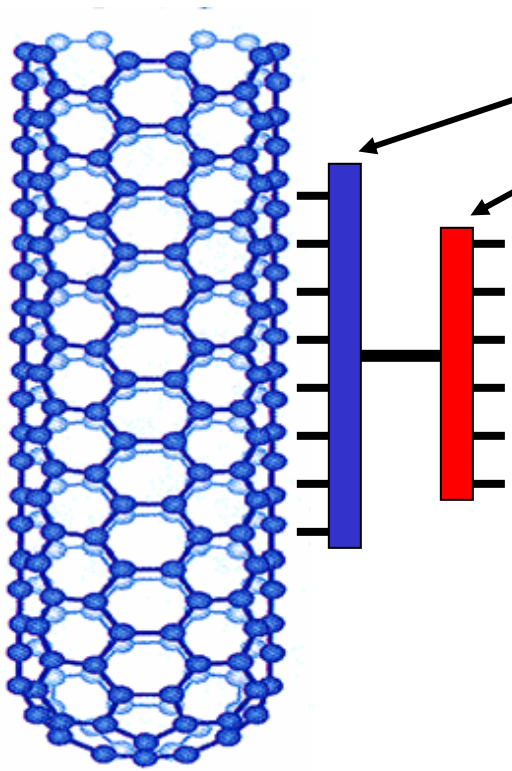


Problems With Pristine Carbon Nanotubes



- Insoluble in Common Solvents
- Difficult to Functionalize
- Difficult to Manipulate & Assemble
- Mixture of Semiconducting & Metallic Nanoubes

Noncovalent Carbon Nanotube Surface Engineering

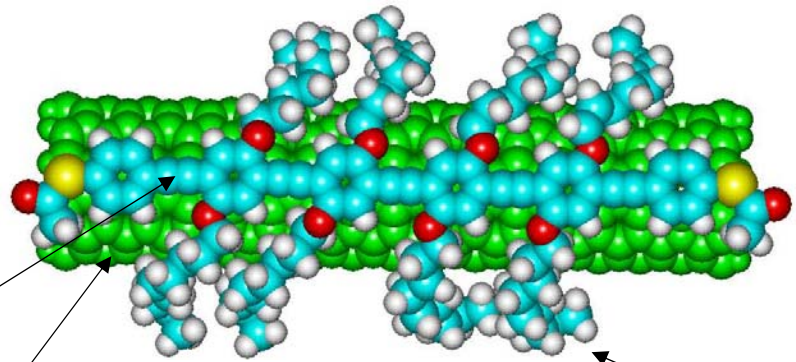


- **Two distinct functions:**
  - Non-damaging binding
  - Designed Multifunctions
- **Binding applicable to SWNTs, MWNTs and other nanostructures**
- **Multifunctions can be engineered for different uses:**
  - Dispersion in various solvents and polymers
  - Adhesion to composite matrix
  - “Wet” manipulation and assembly
  - Separation of metallic from semiconducting carbon nanotubes
  - Functional devices

Noncovalent Carbon Nanotube Surface Engineering

Polymer Non-Wrapping (Zyvex)

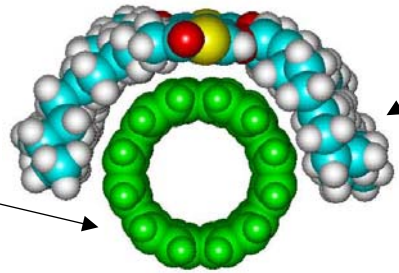
Lateral View



PPE Backbone
(π-π Bonding)

Side Chains
(Functionalization)

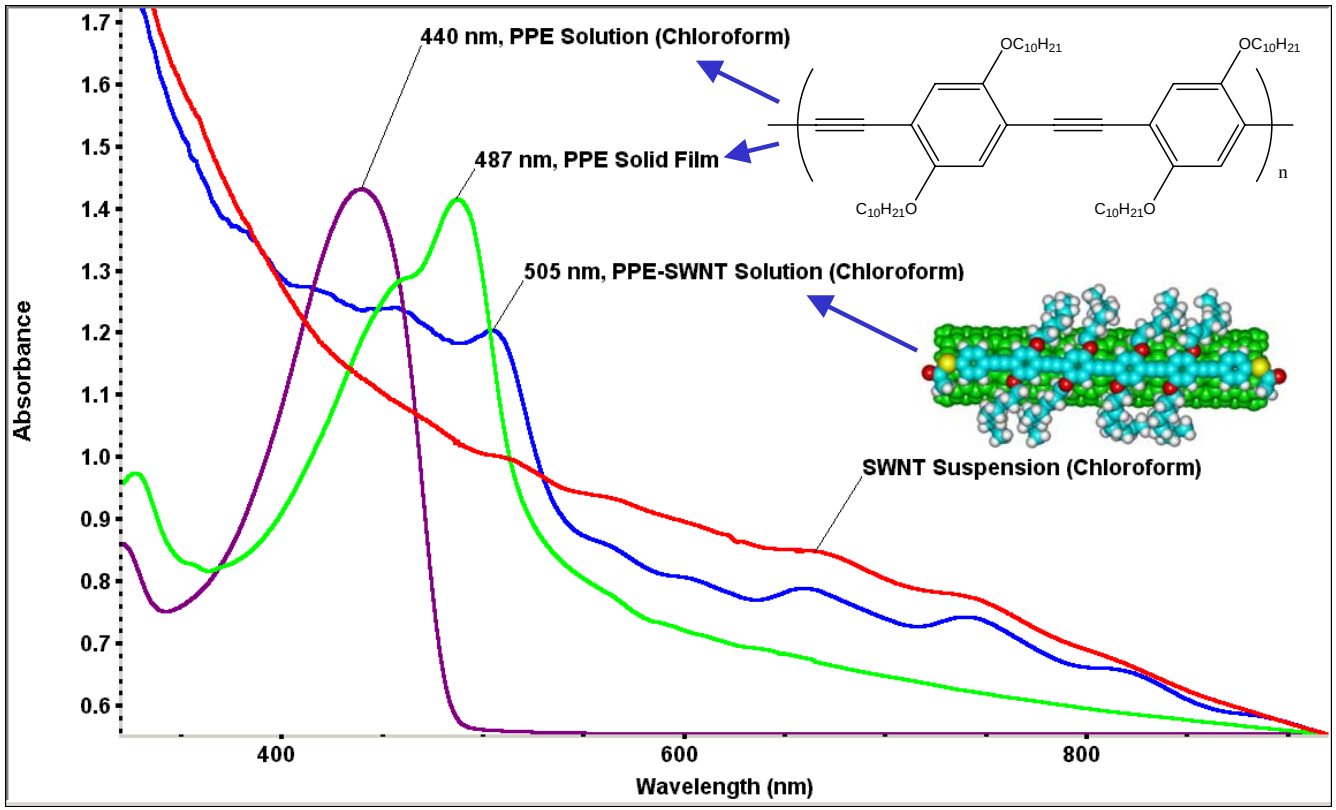
Carbon
Nanotube



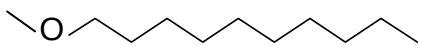
Cross-Sectional View

J. Chen et al. *J. Am. Chem. Soc.* 2002, 124, 9034-9035

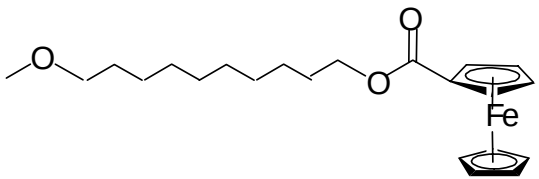
Evidence for PPE Non-Wrapping



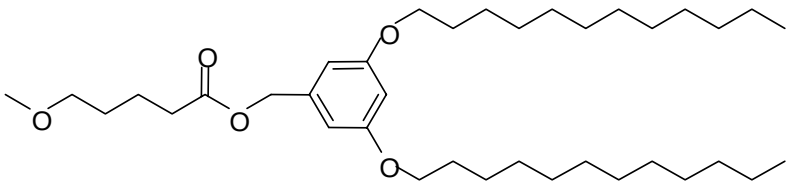
Dissolution of SWNTs



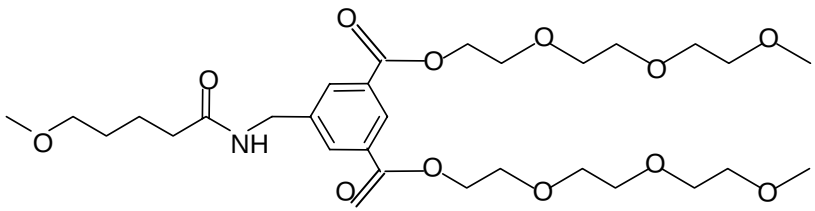
A. Linear Side Chain
up to 2.0 mg/ml in $CHCl_3$



B. Ferrocene termination
up to 5.1 mg/ml in $CHCl_3$



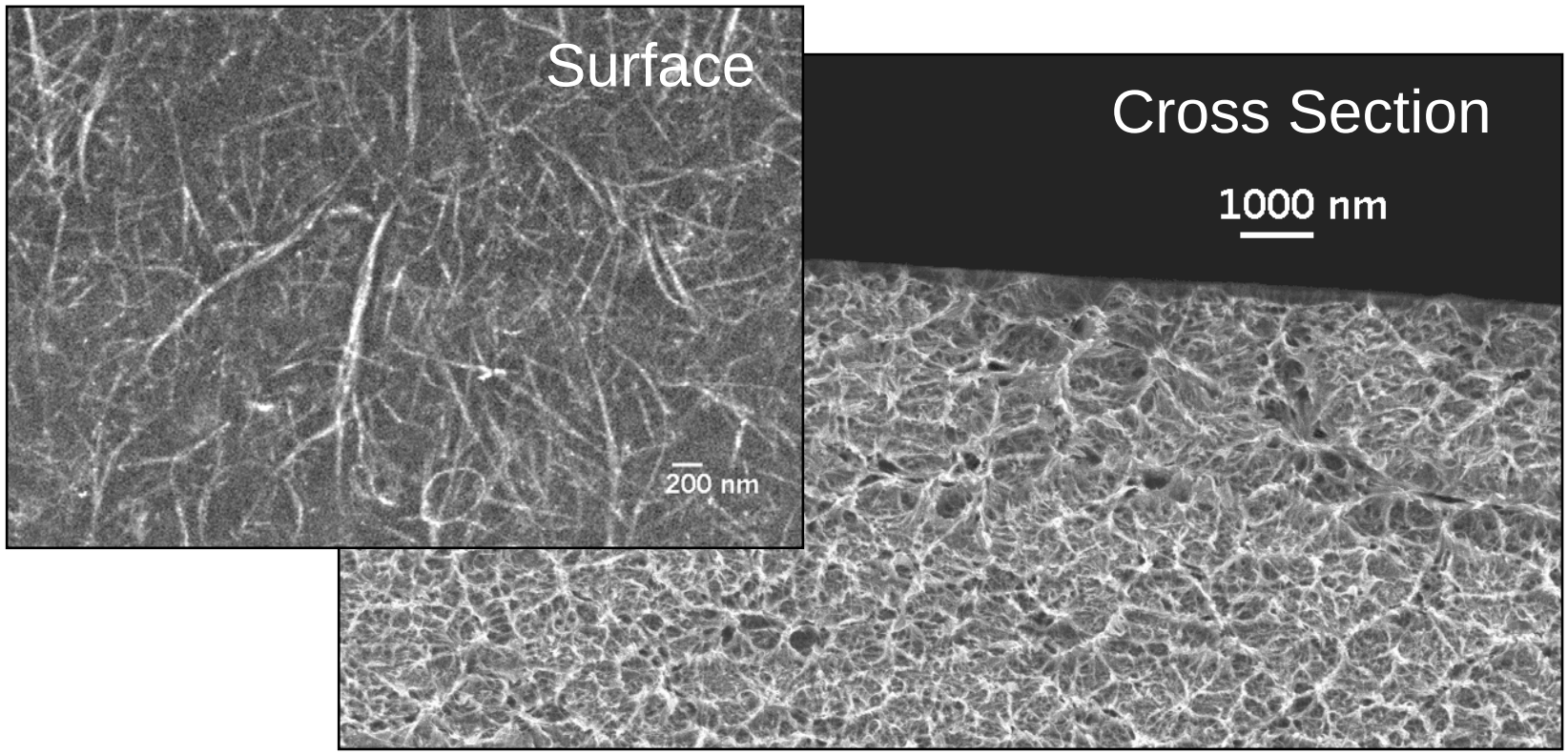
C. Branched Aliphatic Side Chain
up to 8.3 mg/ml in $CHCl_3$



D. Branched Glycol Side Chain
up to 10 mg/ml in NMP
Also soluble in DMF, THF, $CHCl_3$, chlorobenzene *etc.*

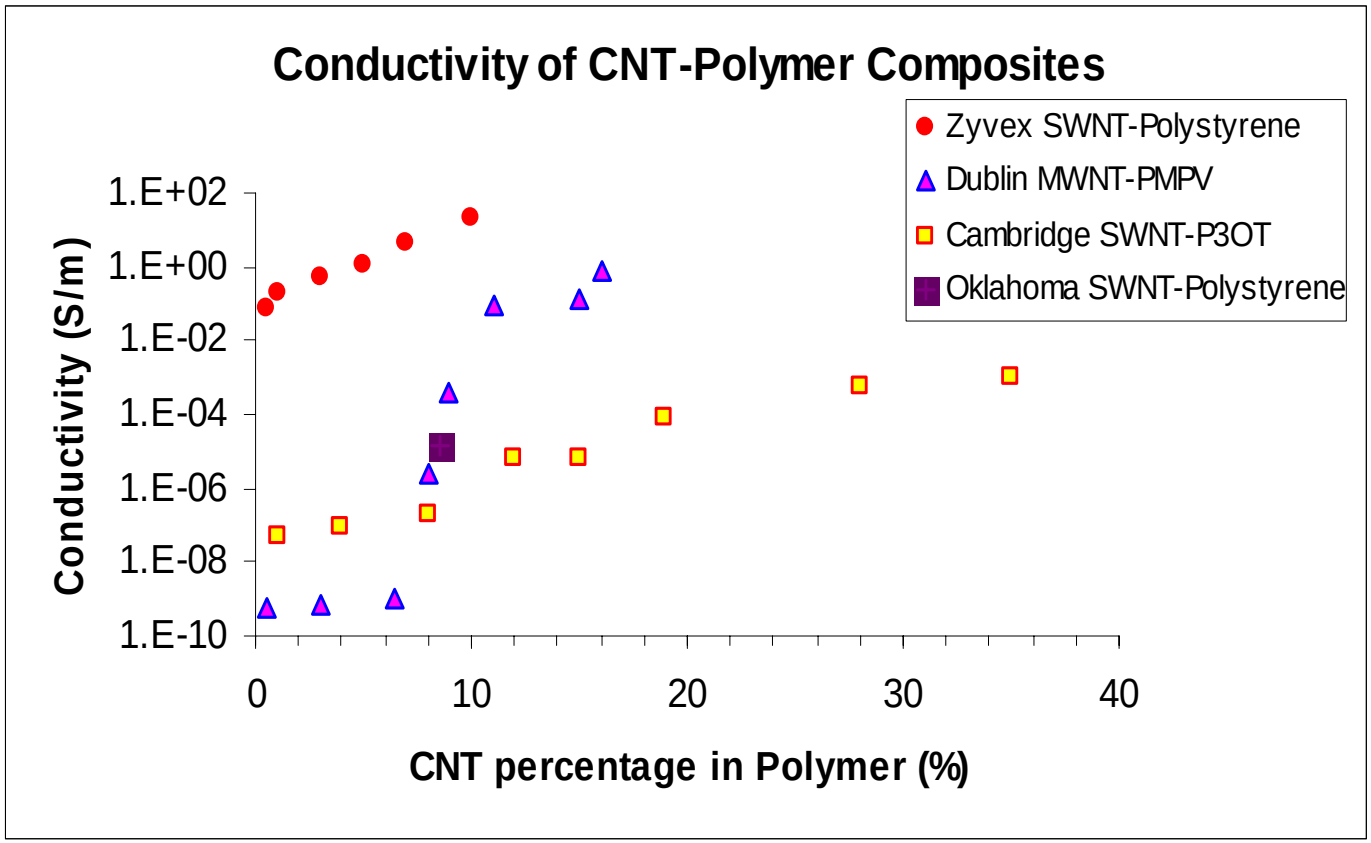
SWNT Dispersion in Polymer Matrix

SWNTs (5 wt%)/Polystyrene Composites



R. Ramasubramaniam et al. Appl. Phys. Lett. 2003, 83, 2928-2930

Electrical Conductivity



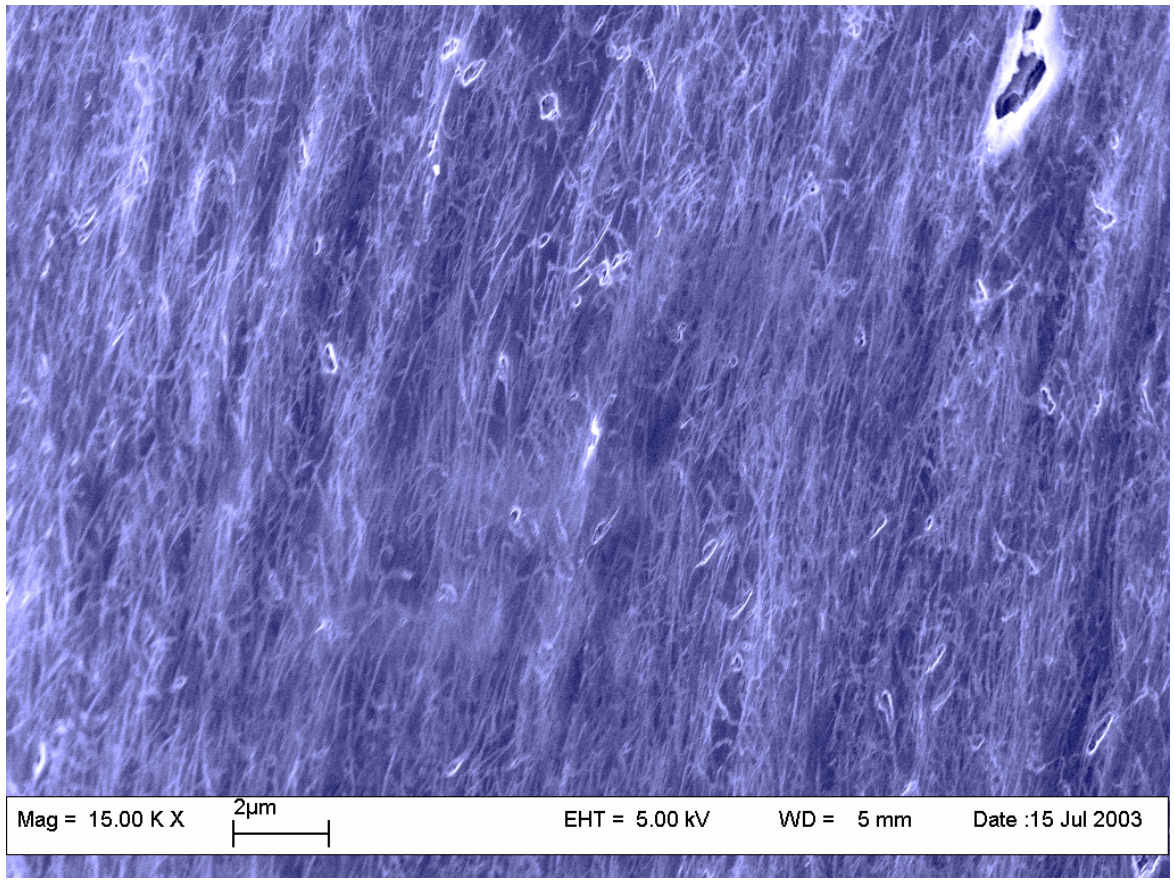
Mechanical improvements

Electrical and mechanical properties of PPE-SWNTs/Polymer composite films

SWNT Loading (wt%)	SWNT Type	PPE Type	Electrical Conductivity (S/m)	Young's Modulus (GPa)	Engineering Tensile Strength At Break (MPa)	True Tensile Strength At Break (MPa)
0	**N/A**	**N/A**	**10^{-14}-10^{-13}**	**3.9**	**154**	**187**
2	r-SWNTs$_{HiPco}$	s-PPE	0.19	4.9	221	254
2	p-SWNTs$_{HiPco}$	s-PPE	0.42	5.6	160	181
2	**p-SWNTs$_{HiPco}$**	**5-PPE**	**To be measured**	**5.1**	**252.5**	**292**
4	r-SWNTs$_{HiPco}$	s-PPE	0.68	4.9	176.5	202
5	p-SWNTs$_{HiPco}$	s-PPE	14.6	6.5	206	221.5
5	**p-SWNTs$_{HiPco}$**	**5-PPE**	**To be measured**	**4.7**	**231**	**272**

Stress-Induced SWNT Alignment in Polymer Matrix

PPE-SWNTs$_{CNI}$ (2 wt%)/Polycarbonate: Good CNT/Polymer Interfacial Interactions

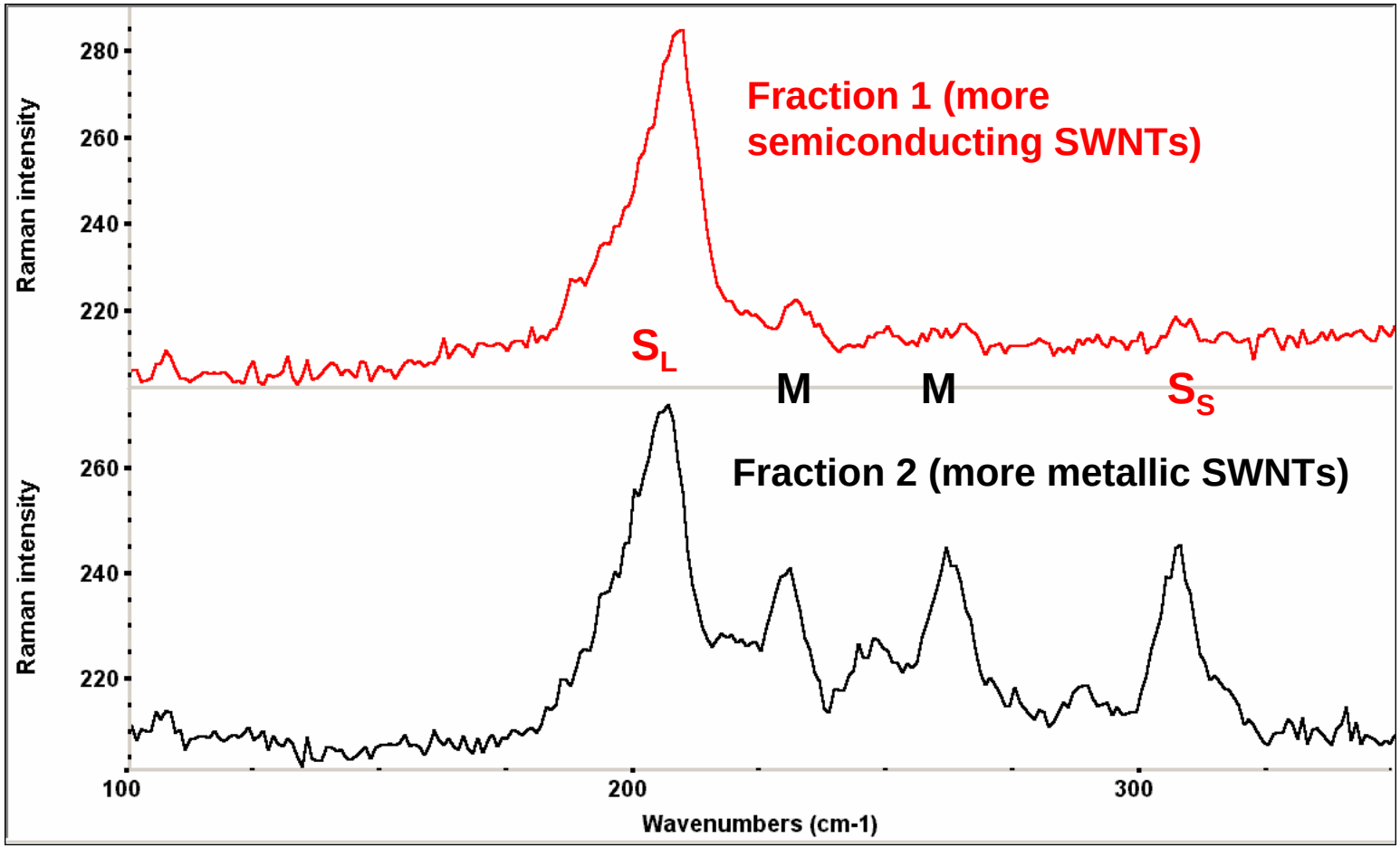


CNT Materials Requirements

- Need control of CNT structures
  - Wide variety of CNT production methods.
  - Narrow distribution of diameters
  - Separation of semiconducting from metallic
  - Single CNT structure process (Smalley)
  - Perfect Carbon Nanotubes?

- Continuous CNT fibers
  - Replacement for PAN Carbon Fibers
  - Spun CNT fibers (Baughman at UTD)

Towards Large Scale Separation of Metallic and Semiconducting SWNTs



Raman Spectra at 488 nm (2.54 eV) excitation

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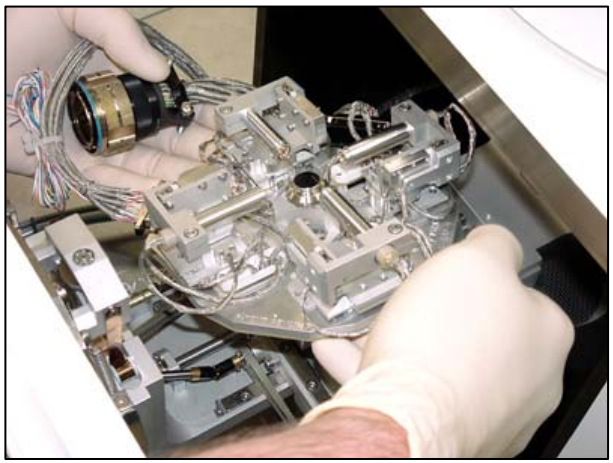
NanoMaterials Metrology & Analysis

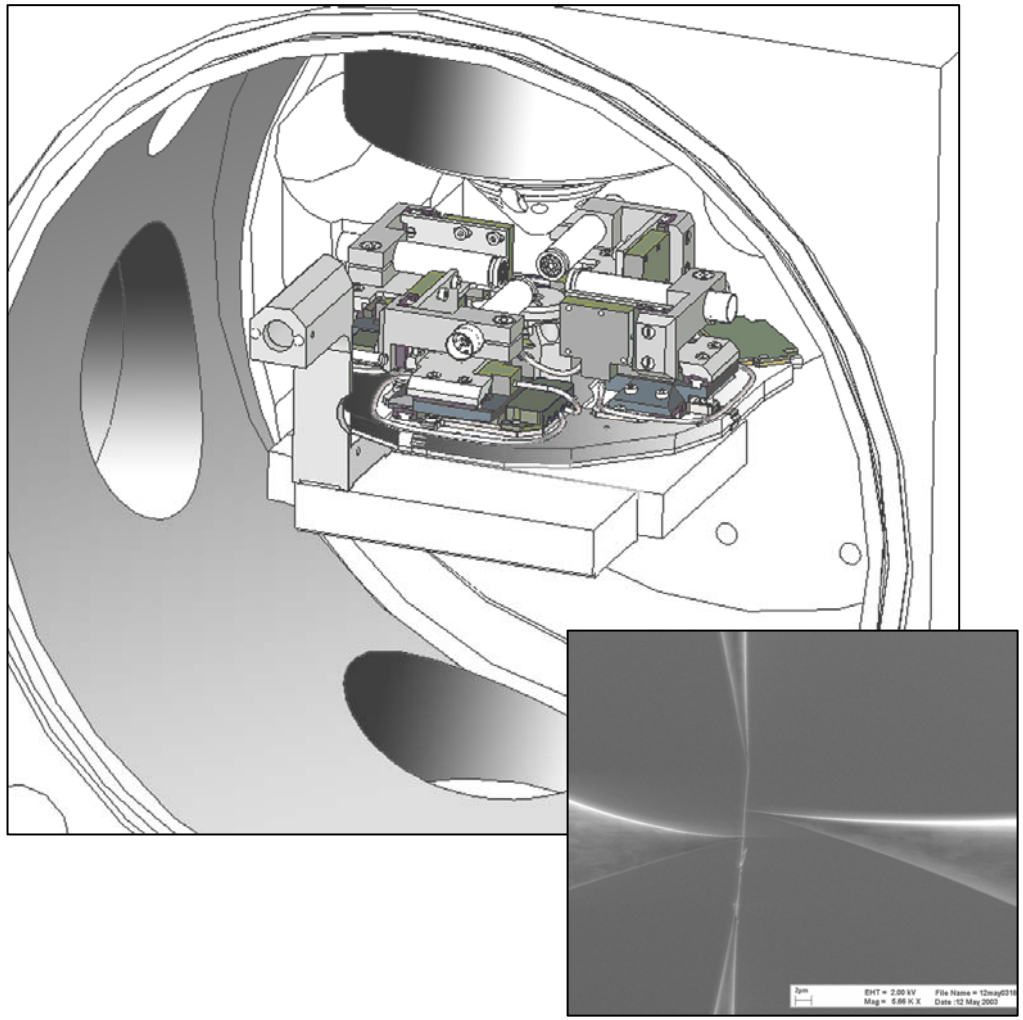
- Need standardized CNT qualification process
  - Determining CNT structure (Weisman at Rice)
  - Diameter measurements (TEM & AFM)
  - Length measurements (No good approaches)

- Measurements of individual CNT properties
  - Nanomanipulation Tools (Zyvex)

- Need better understanding of Nanocomposites
  - Simulations (Wang at FAMU-FSU)
  - Experiments (Drzal at MSU)
  - Nanotube-Matrix interface

S100 Nanomanipulator System





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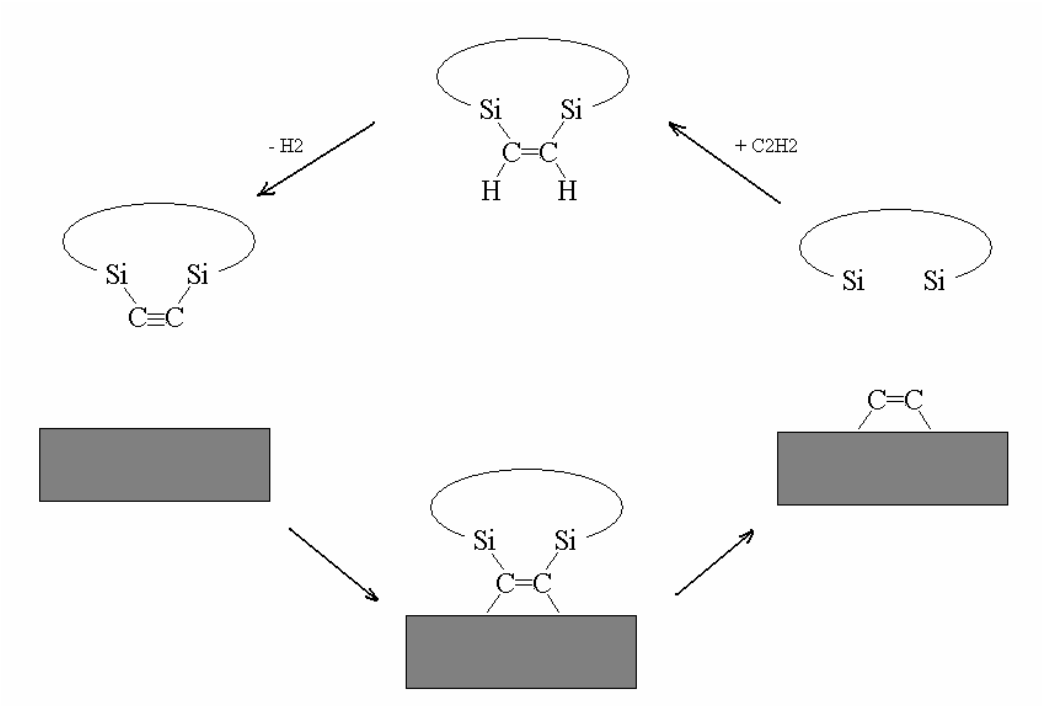
Atomically Precise Manufacturing

Atomically Precise Manufacturing

- IC processing is now in production with tens of nms lateral resolution, and ~1nm film thicknesses.
- It has been 15 years since Don Eigler demonstrated that atoms could be used for public relations gimmicks.
- NIST has an Autonomous Atom Assembler.

- It is time to take advantage of the fact that matter is quantized.
- **We want to take nanofabrication out of the analog game and go <u>DIGITAL</u>.**

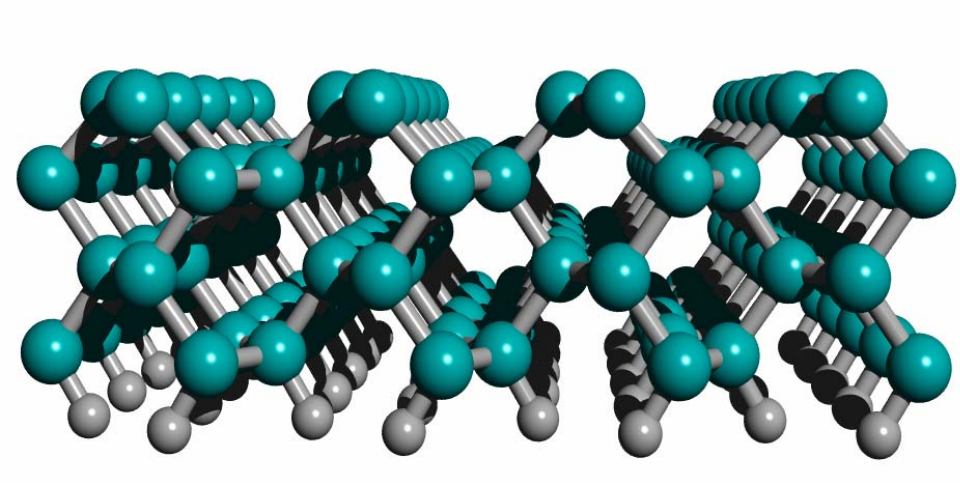
Diamond MechanoSynthesis



Robert A. Freitas Jr., Ralph C. Merkle, **Manufacturing Systems for Molecular Nanotechnology, Volume II: Diamond Surfaces**

Ralph C. Merkle, "**A proposed 'metabolism' for a hydrocarbon assembler**," Nanotechnology 8(1997):149-162

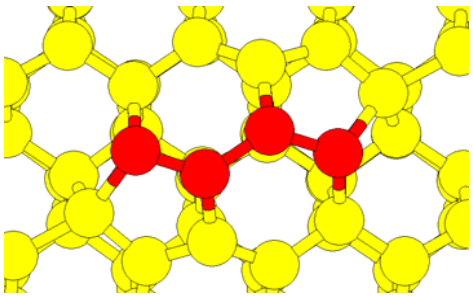
Diamond 110 Surface



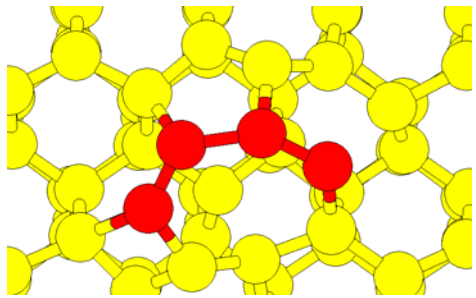
Unlike 111 and 100 surfaces the hydrogen depassivated diamond 110 surface does not reconstruct and is the most chemically inert.

Diamond Surface Chemistry

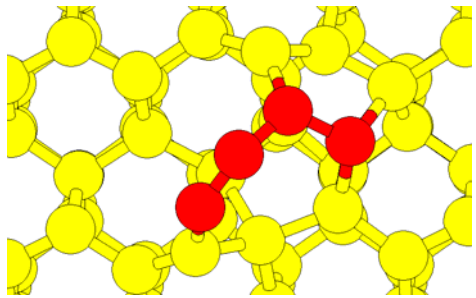
Density Functional Theory (DFT) with generalized gradient approximation (GGA) by constructing the reaction path potential energy profiles and analyzing *ab initio* molecular dynamics simulations.



A (native structure)



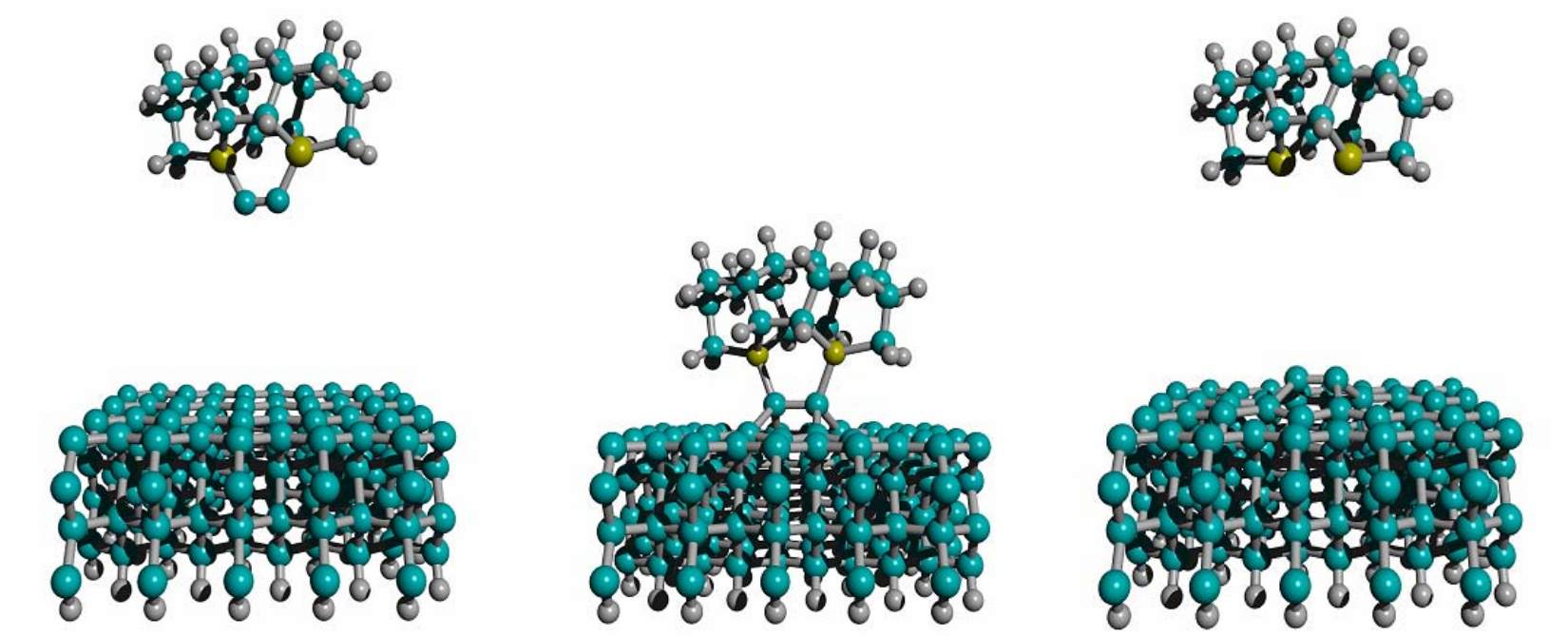
D-1 (defect structure)



D-2 (defect structure 2)

2 Dimers: 19 local minima, 5 of which are stable defects

Tool+Substrate Chemistry

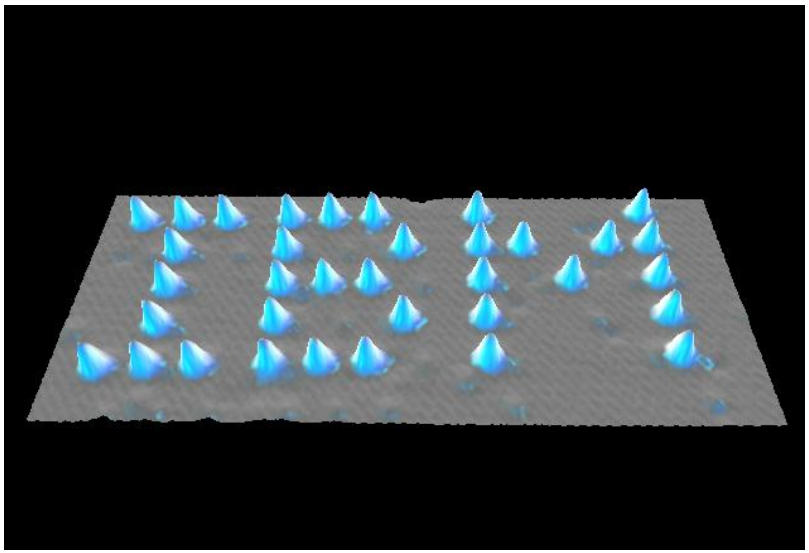


Si/Ge-triadamantane tools

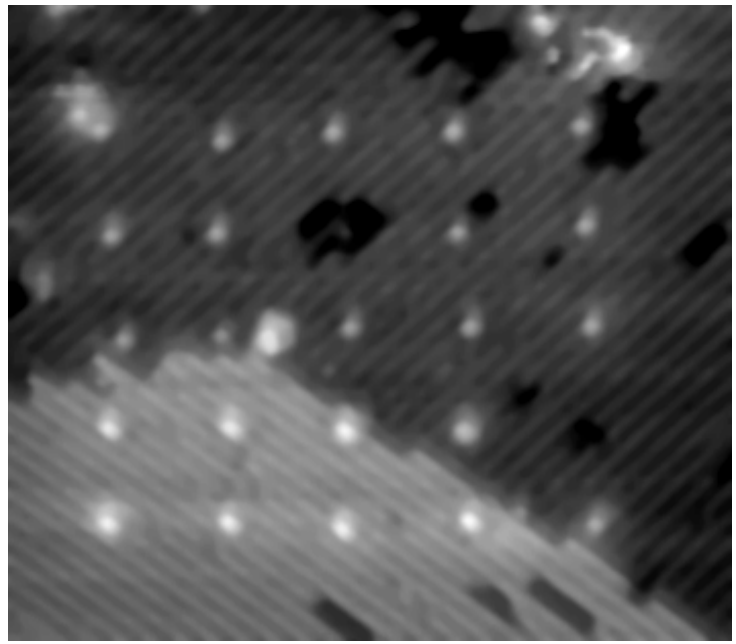
THE Problem

We do not have atomically precise tools.

Atomic Precision 2D



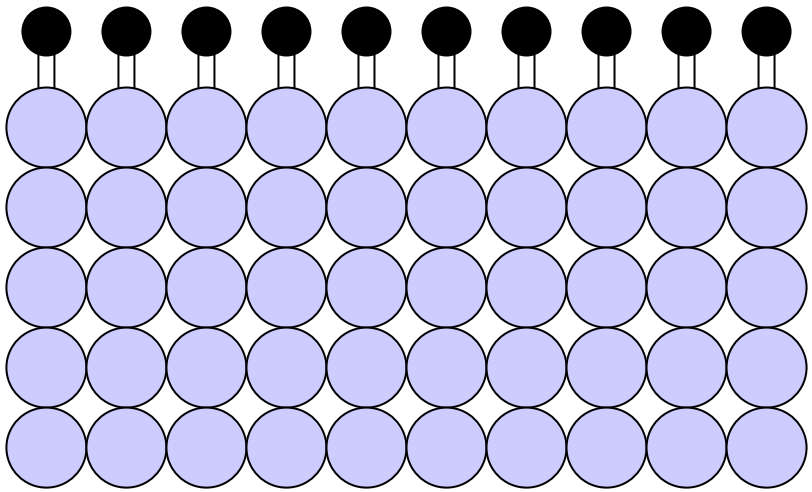
1989: Xenon on Nickel (110)



Single H atoms programmably removed from a Si 100 surface by Hersham and Lyding using their STM depassivation technique.

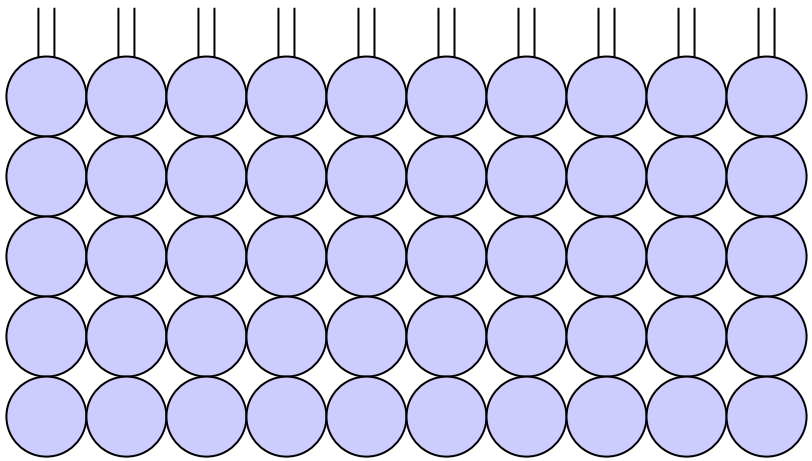
Atomic Layer Epitaxy/Deposition

Start with passivated surface



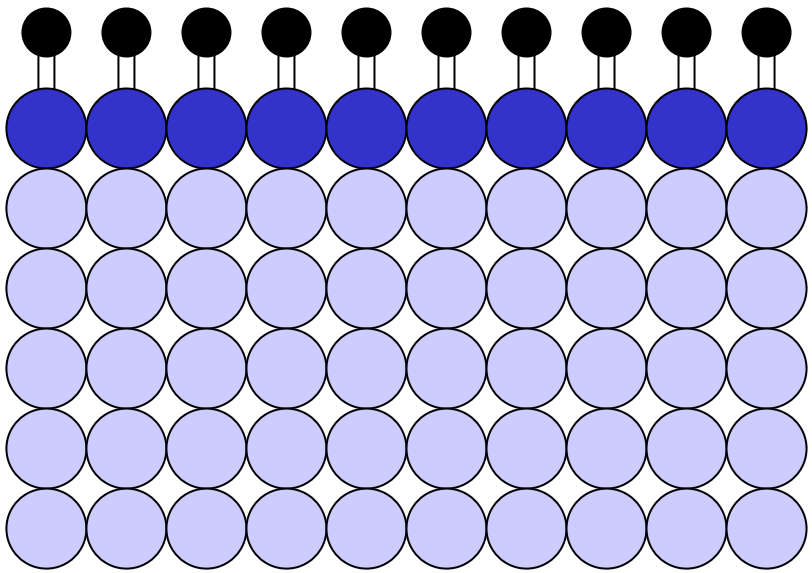
Atomic Layer Epitaxy/Deposition

Process surface to activate for bonding



Atomic Layer Epitaxy/Deposition

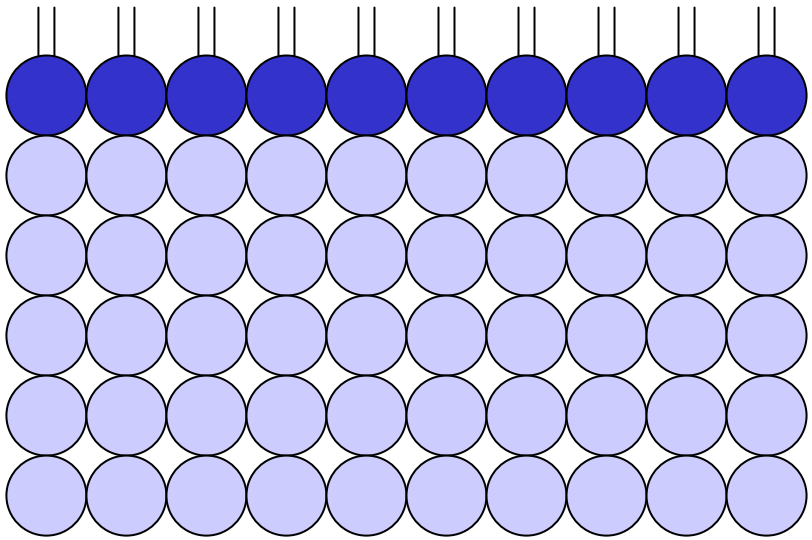
Self-limiting deposition of monolayer



Blocking Chemistry

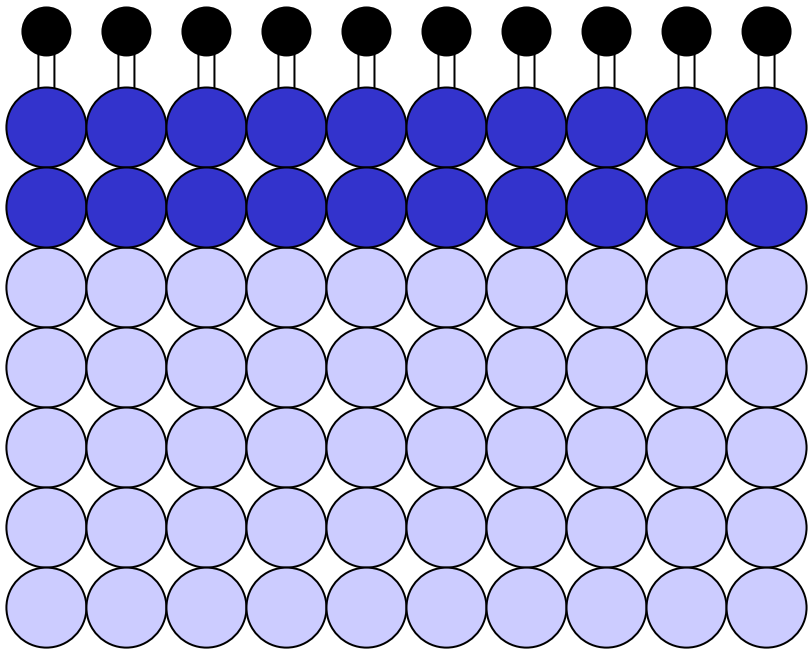
Atomic Layer Epitaxy/Deposition

Removal of blocking chemistry



Atomic Layer Epitaxy/Deposition

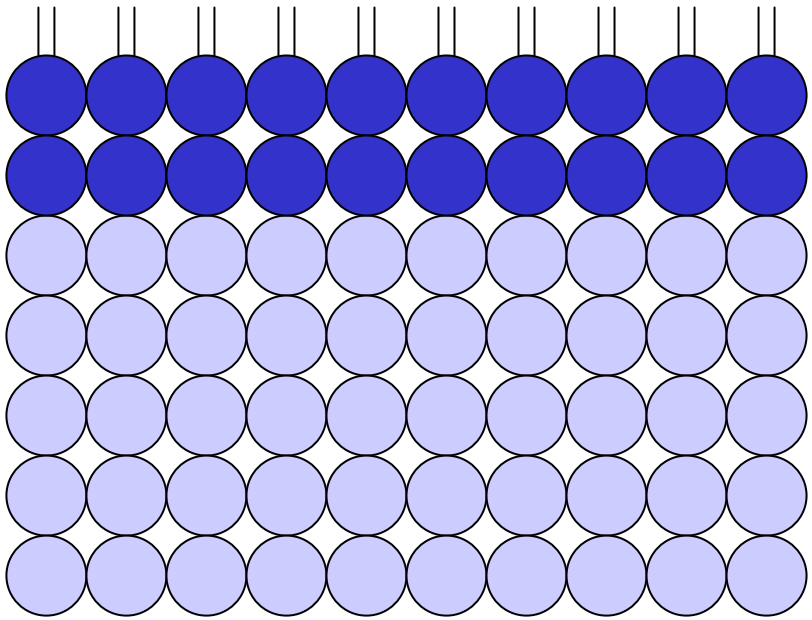
2nd self-limiting deposition of monolayer



Blocking Chemistry

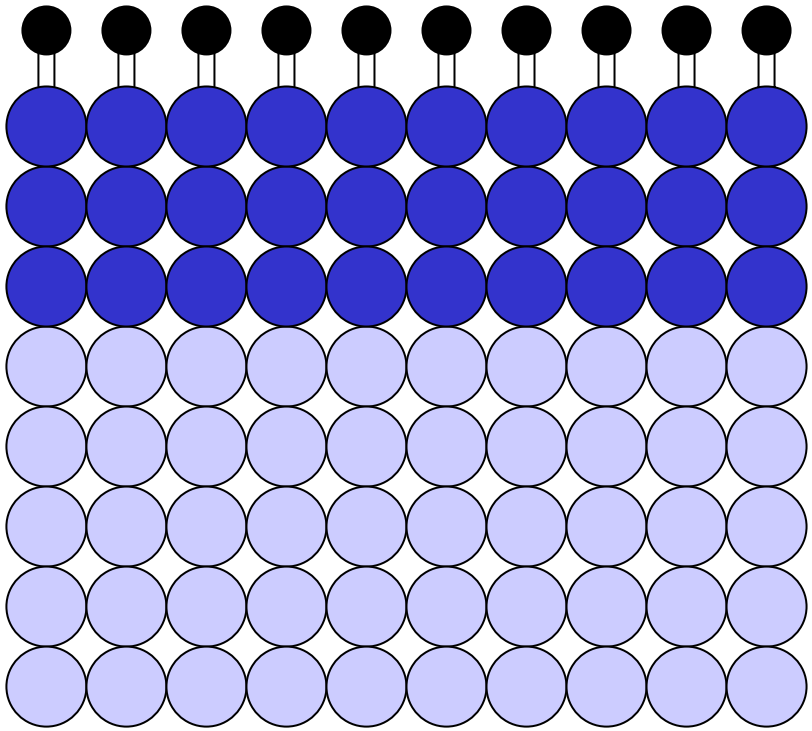
Atomic Layer Epitaxy/Deposition

Removal of blocking chemistry



Atomic Layer Epitaxy/Deposition

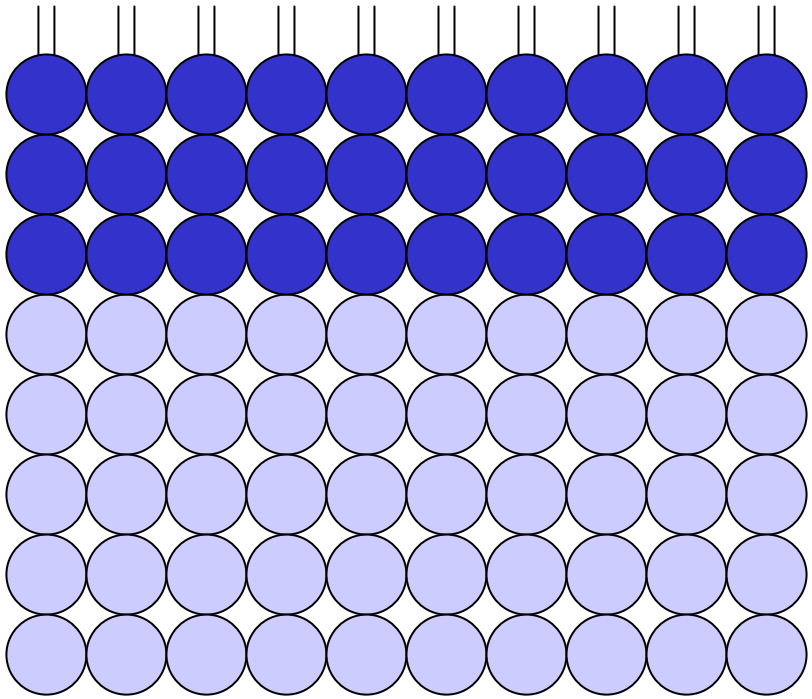
Etc.



Blocking Chemistry

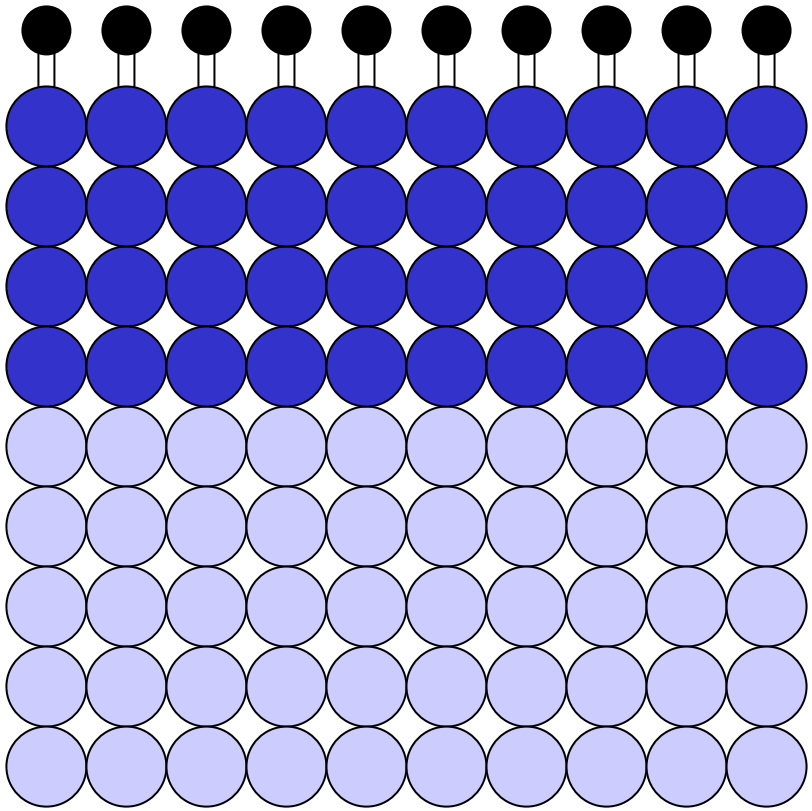
Atomic Layer Epitaxy/Deposition

Etc. Etc.



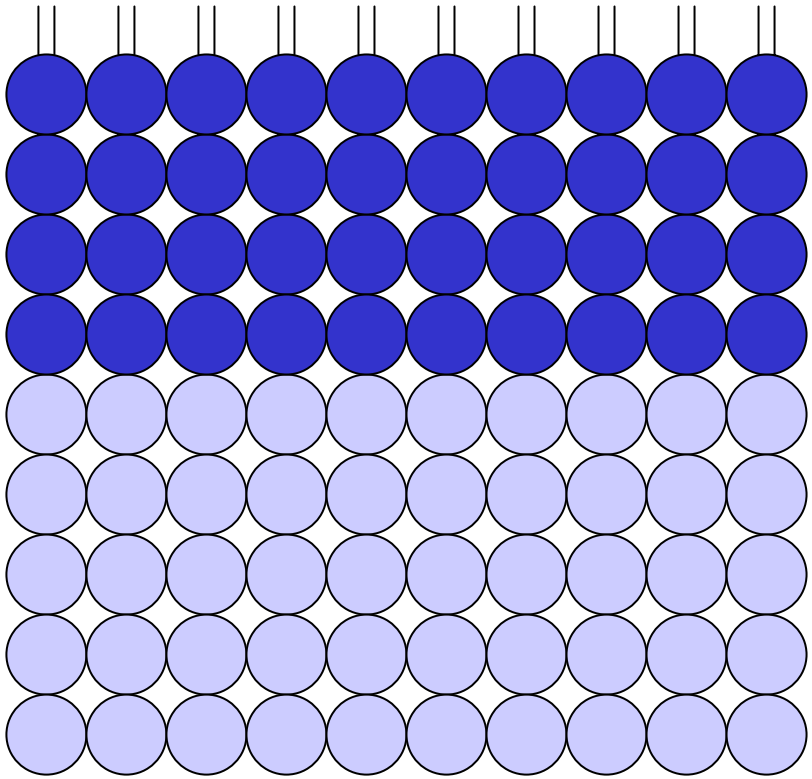
Atomic Layer Epitaxy/Deposition

Etc. Etc. Etc.



Atomic Layer Epitaxy/Deposition

Etc. Etc. Etc. Etc.

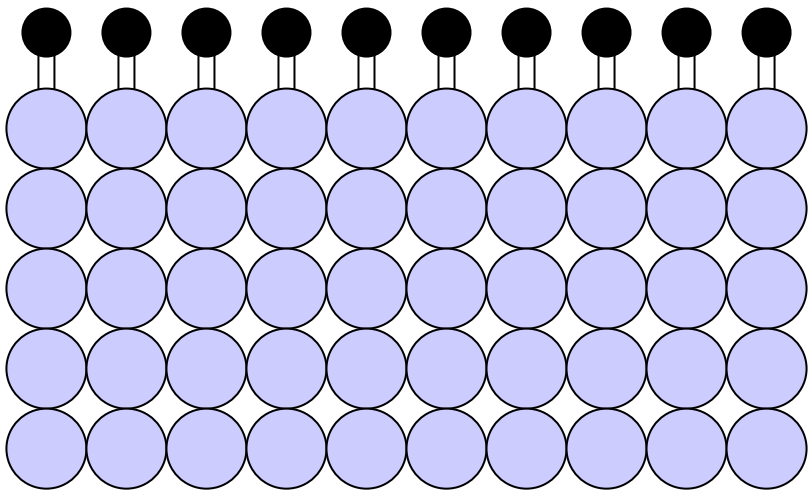


ALE/ALD material systems

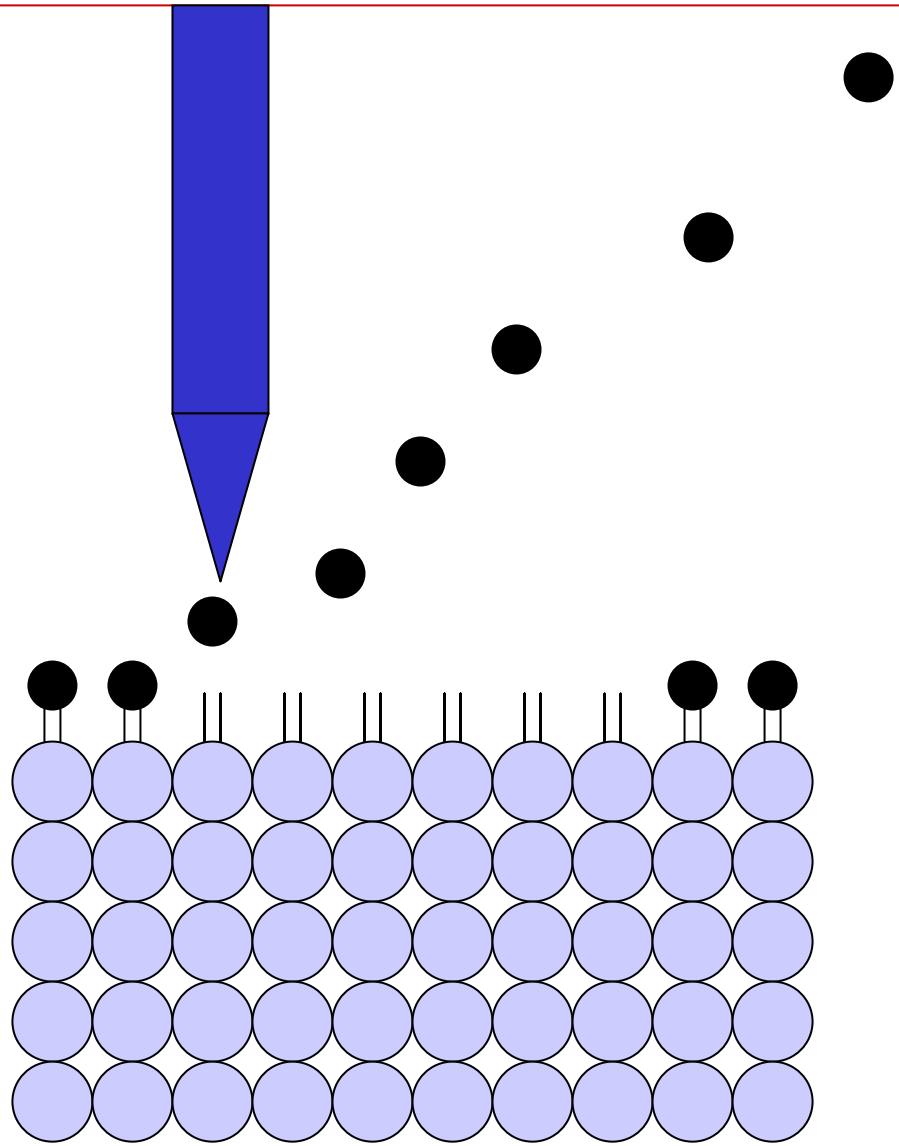
II–VI compounds	ZnS, $ZnSe$, $ZnTe$, $ZnS_{1-x}Se_x$
	CaS, SrS, BaS, $SrS_{1-x}Se_x$
	CdS, $CdTe$, $MnTe$, $HgTe$, $Hg_{1-x}Cd_xTe$, $Cd_{1-x}Mn_xTe$
II–VI based TFEL phosphors	ZnS:M (M = Mn, Tb, Tm), CaS:M (M = Eu, Ce, Tb, Pb)
	SrS:M (M = Ce, Tb, Pb, Mn, Cu)
III–V compounds	$GaAs$, $AlAs$, AlP, InP, GaP, $InAs$
	$Al_xGa_{1-x}As$, $Ga_xIn_{1-x}As$, $Ga_xIn_{1-x}P$
Nitrides	
Semiconductors/Dielectric	AlN, GaN, InN, SiN_x
Metallic	TiN, TaN, Ta_3N_5, NbN, MoN
Oxides	
Dielectric	Al_2O_3, TiO_2, ZrO_2, HfO_2, Ta_2O_5, Nb_2O_5, Y_2O_3, MgO, CeO_2, SiO_2, La_2O_3, $SrTiO_3$, $BaTiO_3$
Transparent conductors/ Semiconductors	In_2O_3, In_2O_3:Sn, In_2O_3:F, In_2O_3:Zr, SnO_2, SnO_2:Sb, ZnO, ZnO:Al, Ga_2O_3, NiO, CoO_x
Superconductors	$YBa_2Cu_3O_{7-x}$
Other ternaries	$LaCoO_3$, $LaNiO_3$
Fluorides	CaF_2, SrF_2, ZnF_2
Elements	Si, Ge, Cu, Mo
Others	La_2S_3, PbS, In_2S_3, $CuGaS_2$, SiC

Patterned Deposition

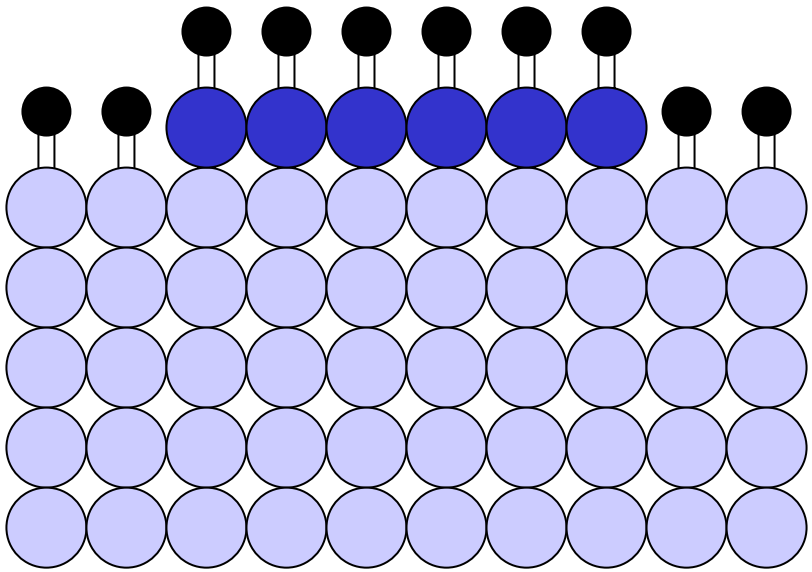
Start with passivated surface



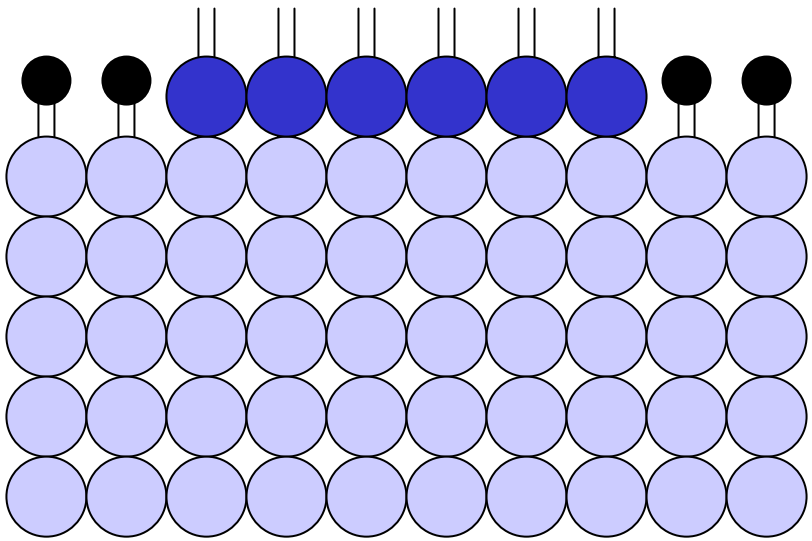
Patterned depassivation



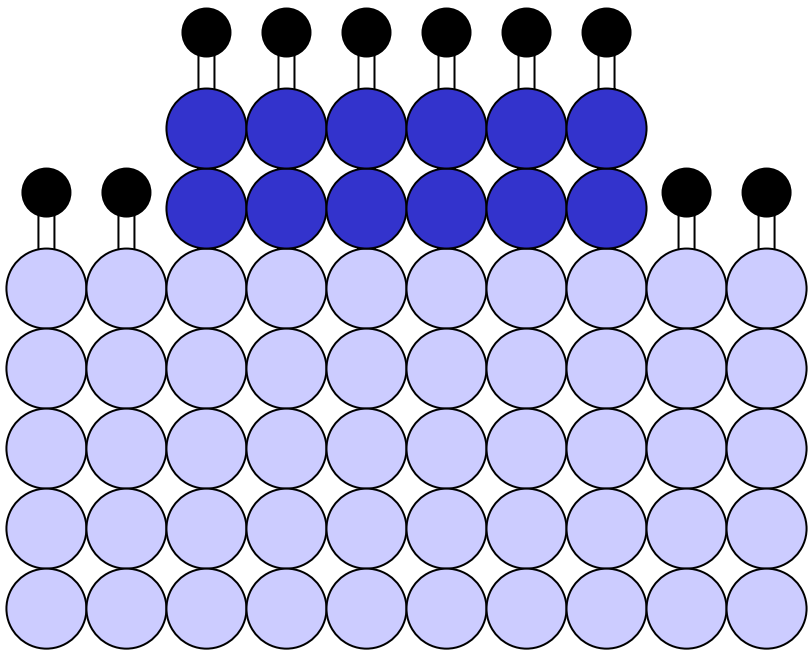
Selective deposition



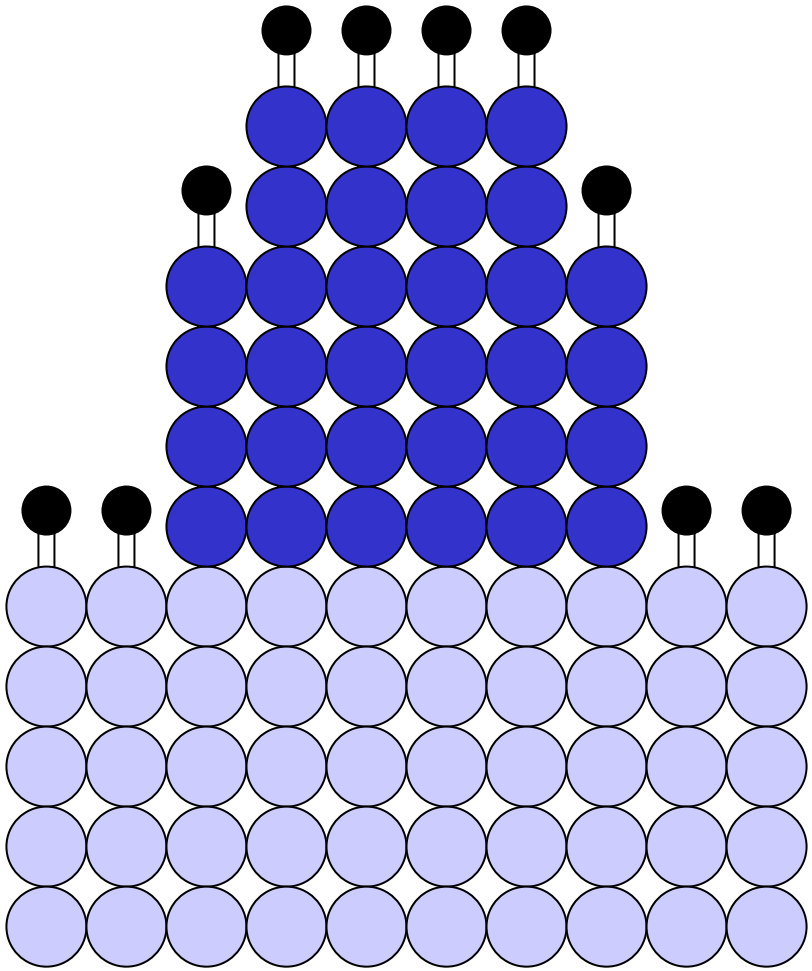
Patterned depassivation



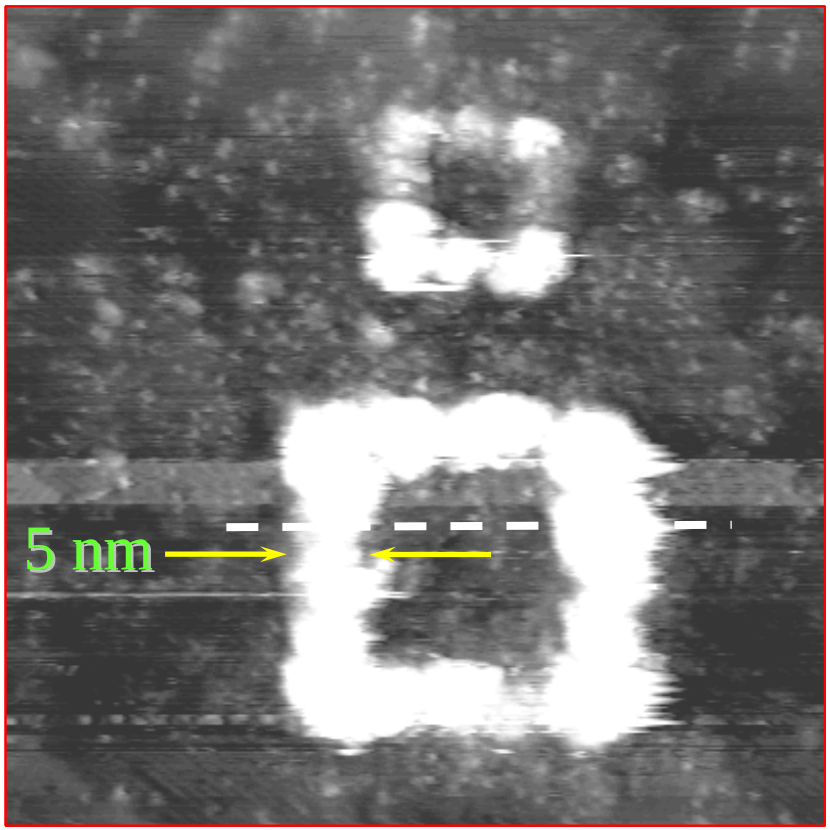
Selective deposition

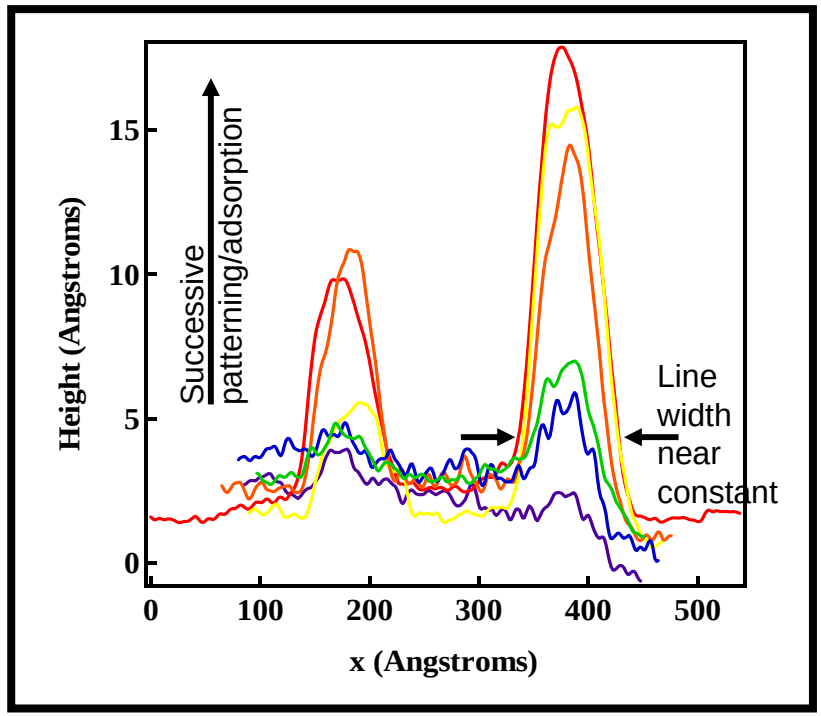


3D Structure



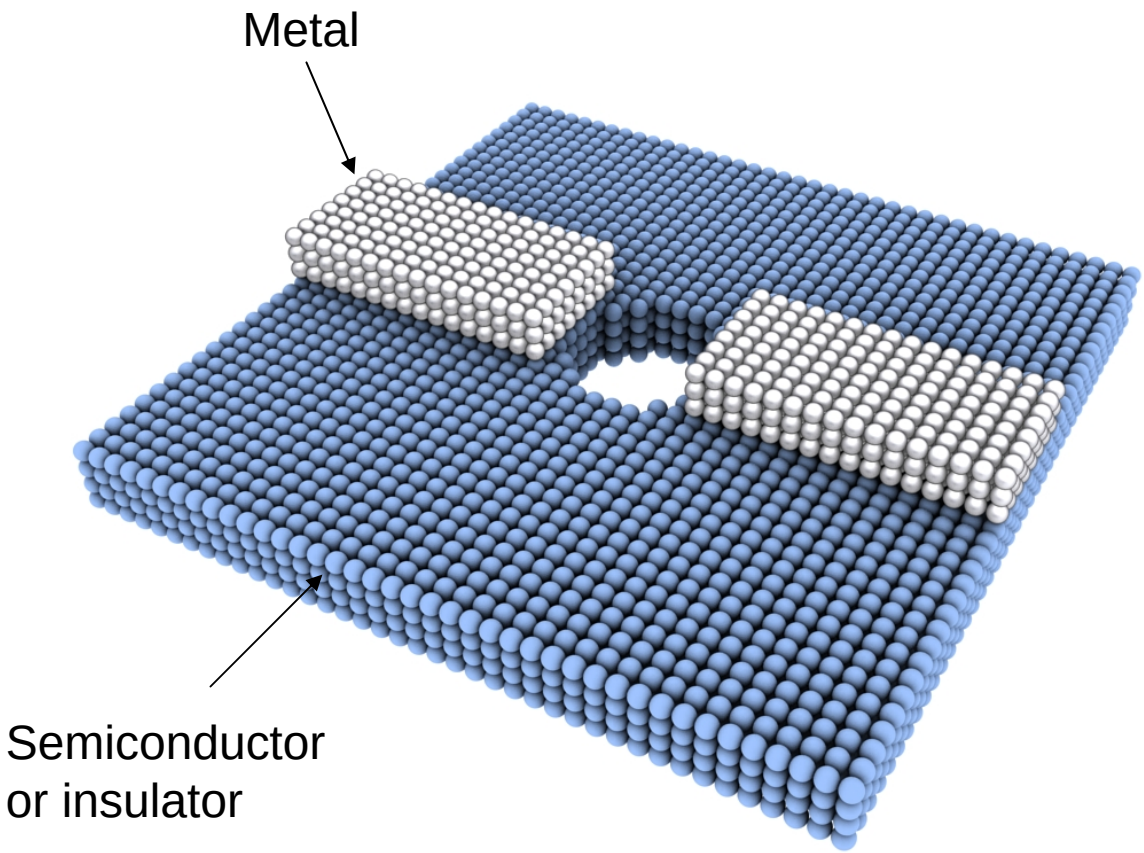
First Demonstration of Patterned Si ALE





Work by Joe Lyding UIUC

Nanopore with integrated electrodes.

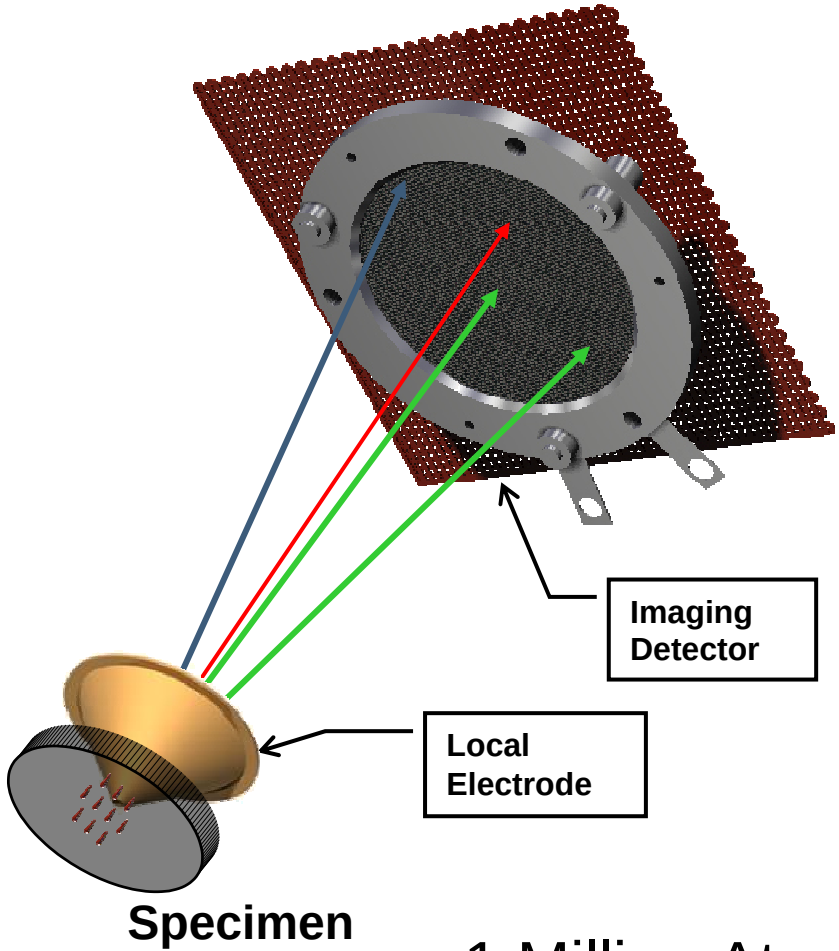


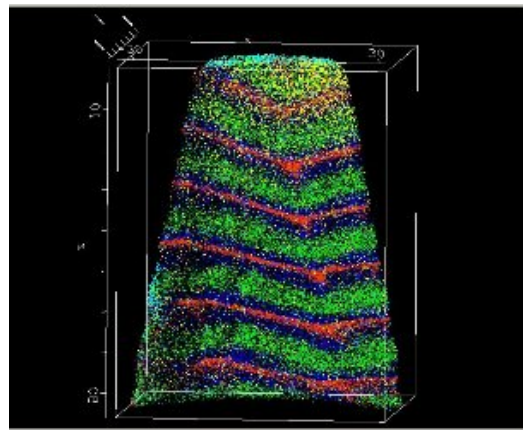
A Nanopore could be used to sequence single starnds of DNA at 1000 bases per second.

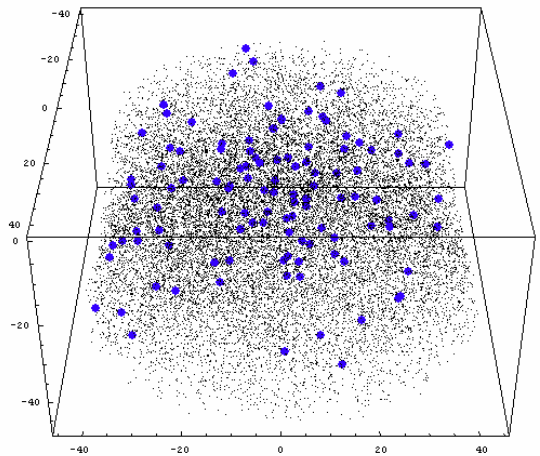
Metrology Requirements

- Atomically precise manufacturing will require metrology with atomic precision.
  - Scanning probes have atomic resolution but terrible accuracy.
  - Rick Silver's (NIST) interferometer can help the accuracy.
  - The imprecision of SP tips is a major problem.
  - Scanning probes are generally limited to 2D structures.
  - Dan Rugar (IBM) scanning NMR has 3D possibilities.

Imago's Atom Probe







1 Million Atoms

Material Requirements

- ULTRA High Purity feedstock materials.
- Better understanding of surfaces at the atomic scale.
- Passivation layers.

General Questions

- What is considered state-of-the-art, in terms of experiment/ processing/ characterization **and/or** theory/ modeling? (this may include some of your own work)
- What are the problems now under investigation?
- What barriers (scientific and/or technological) do you foresee to advances in the coming 5 to 10 years? Please include barriers that may be addressed by improvements in materials measurements.

- See previous 70 slides.

General Questions

- What are possible approaches to solution? Please include how you might envision “division of labor,” i.e. roles of industry, DOE labs, NIST, universities.
  - NIST plays a critical role in metrology and material characterization.
  - Universities are being asked to do a lot of research that is NOT fundamental. <u>This is good and bad.</u>
  - More industrial research is essential.
  - Division of labor will be determined by market forces as well as policy.
  - It is important to keep market forces alive in the US.

Questions for Fabrication Speakers

- How is mechanics/mechanical behavior important in terms of performance and reliability required at product level?
  - Micro and nano mechanical properties are going to be exploited in many technological applications:
  - Already: SAW devices, DLP, accelerometers,
  - Soon: Microfluidics, Sensors, NEMS
  - Eventually: Complex machinery at nanoscale

Questions for Fabrication Speakers

- How do you design-in performance and reliability, using principles of micro- and nanostructure control?
  - Modeling and lots of it.

- Please comment on adequacy of existing lifetime or performance prediction methods.
  - Adequate for Si.
  - A long way to go for other materials.
  - Material parameters and nanoscale effects need improved understanding.

Questions for Fabrication Speakers

- How does industry measure performance of both the end product and the constituent materials?

- What are the limitations/barriers of the present measures/metrology?
  - Better understanding on nanostructures and nanocomposites needed.
  - Most metrology is stuck in 2D
  - Need atomically precise metrology
  - Need atomically precise tools

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Hierarchical Composites Comprising Continuous Carbon Nanotube Composite Fibers in a Nanotube-Reinforced Matrix

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DOE SBIR Phase I

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