Introduction to Nanotechnology

- Textbook：

  Nanophysics and Nanotechnology

  by:

  Edward L. Wolf

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Classroom: A209
Time: Thursday; 13:20-16:10 PM
Office hour: Thur., 10:00-11:30 AM or by appointment

Sep 15	Introduction	Hossein
Sep 22	Systematic of Making Things Smaller	Hossein
Sep 29	What are limits to smallness	Hossein
Oct 6	Quantum Nature of the Nanoworld	CW Chen
Oct 13	Quantum Consequence for the Macroworld	CW Chen
Oct 20		
Oct 27	Self-Assmbled Nano-Straucture in Nature and Industry	Hossein
Nov 3		
Nov 10	**Midterm**	
Nov 17	Physics-based Experimental Approaches to Nanofabrication and Nanotechnology	Hossein
Nov 24		
Dec 1	Quantum Technologies based on Magnetism, Electron and Nuclear Spin, and Superconductivity	KH Chen
Dec 8		
Dec 15	Silicon Nanoeletronic and Beyond	Hossein
Dec 22		
Dec 29	Looking into the Future	LC Chen
Jan 5		
Jan 11 (2 ~5 pm). 4th floor, C.T Chang Memorial Hall, Con Fourth Floor	**Final Exam**	

Objective of the course

The course, Introduction to Nanotechnology (IN), will focus on understanding of the basic molecular structure principals of Nano-materials. It will address the molecular structures of various materials. The long term goal of this course is to teach molecular design of materials for a broad range of applications. A brief history of biological materials and its future perspective as well as its impact to the society will be also discussed.

Evaluation; Score: 100%:

Mid-term Exam: 30%
Final Exam: 30%
Scientific Activity: 40 % (Home work, Innovation Design)

Contents

- Introduction (*Prof. Hossein*)
- Systematic of Making Things Smaller (*Prof. Hossein*)
- What are limits to smallness (*Prof. Hossein*)
- Quantum Nature of the Nano-world (*Prof. CW Chen*)
- Quantum Consequence for the Macro-world (*Prof. CW Chen*)
- Self-Assembled Nano-Structure in Nature and Industry (*Prof. Hossein*)
- Physical-based Experimental Approaches to Nanofabrication and Nanotechnology (*Prof. Hossein*)

- Mid-term Exam

Contents

- Quantum Technologies based on Magnetism, Electron and Nuclear Spin, and Superconductivity (*Prof. KH Chen*)
- Silicon Nanoeletronic and Beyond (*Prof. Hossein*)
- Looking into the Future (*Prof. LC Chen*)

- Final Exam

Silicon Nanoeletronic and Beyond

Subjects: Today class

1. **Molecular Switch in Nano-electronics**
2. **Nano-sensors**
3. **Detectors**

Question: How to deal with 10 nm Technology and beyond?
Answer: Advanced Device Physics!!

Note: 1. Device Physics devotes to Transport in devices.
2. Low Dimensionality means Quantum Confinement.

Source/Drain Plasmons

C-V/I-V for NanoFETs?? Long-range Coulomb Interaction

Metal gate high-*k*

Soft Phonons

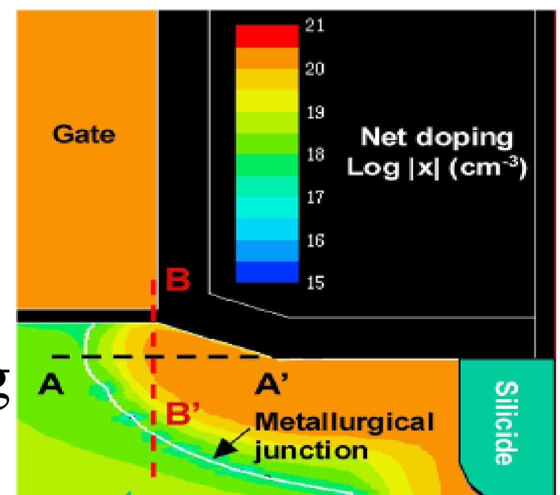
Bulk, SOI, FinFET, nanowire

Strain

Tunneling FETs
for steep subthreshold

DIBL

Tunneling

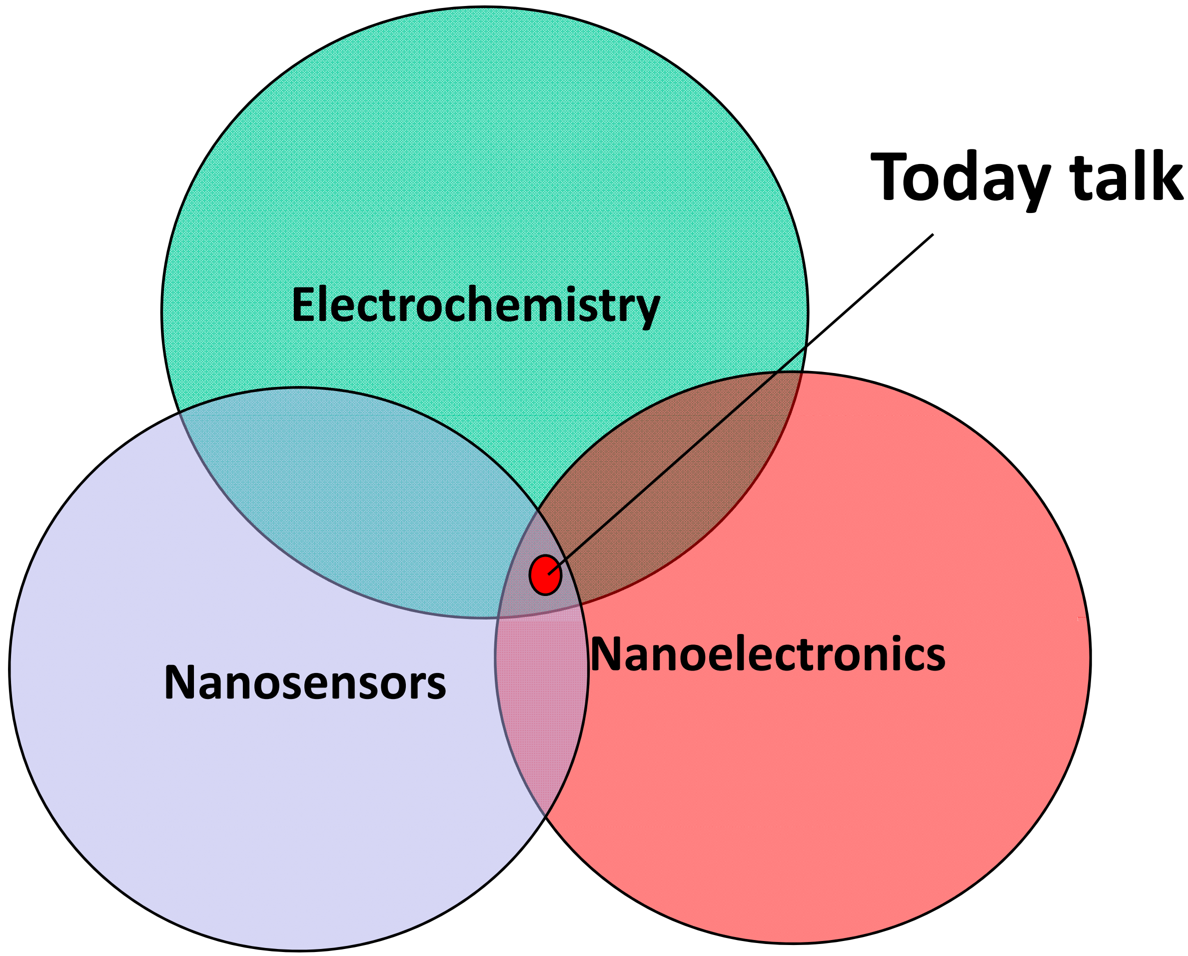


Substrate and Channel Orientation

High mobility graphene as
channel replacement materials

Parasitic effects

Only half of the device is shown.


Today talk
Electrochemistry
Nanosensors
Nanoelectronics

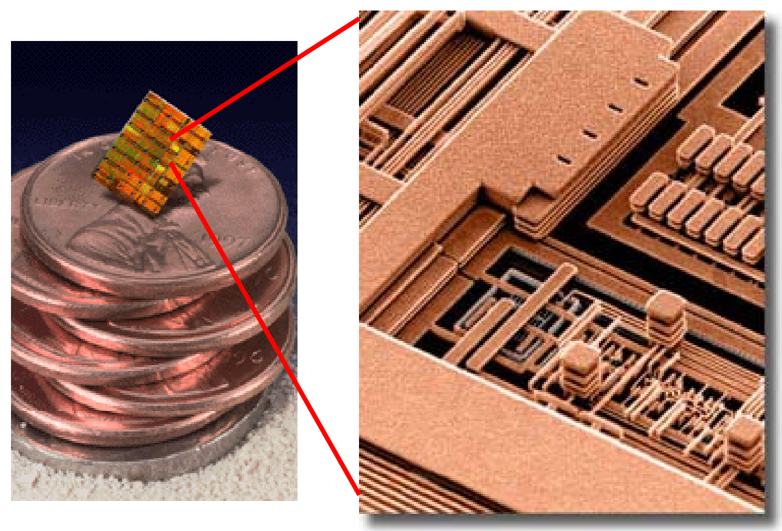
Electrochemical Nanofabrication

- **Electrodeposition & etching**

Electrodeposition: Then … and Now…

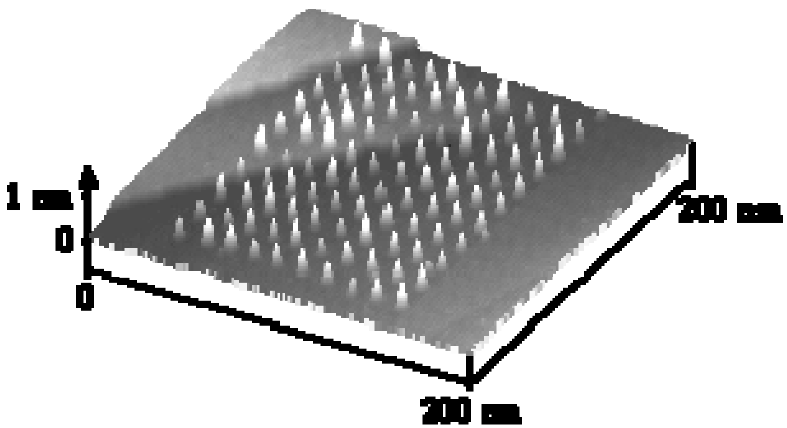
- **Ancient origin.** Romans soldered silver plates to articles of metals and in the 5th century iron weapons were coated with copper by dipping them in a copper solution. During the 18th century, plating of copper or brass with silver by fusion started in England.

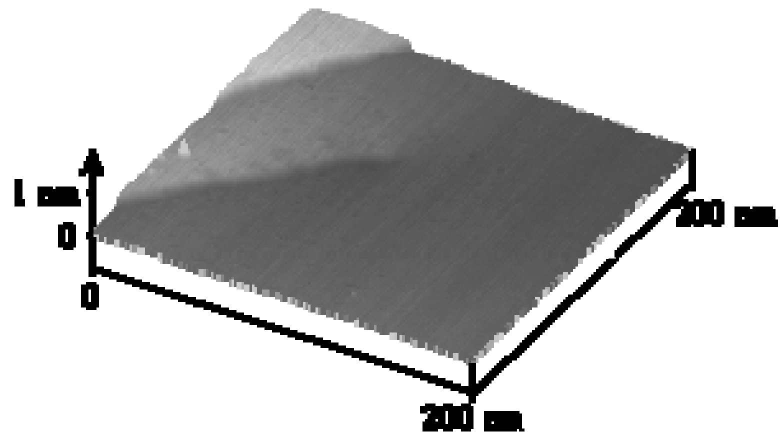
- IBM announced in1997 a new advance in semiconductor process that entails replacing aluminum with copper. Cu has less "resistance" than Al.



Local Probe Approach (STM & AFM)

The clusters can be dissolved by changing the sample potential and afterwards the blank Au surface can be imaged again.



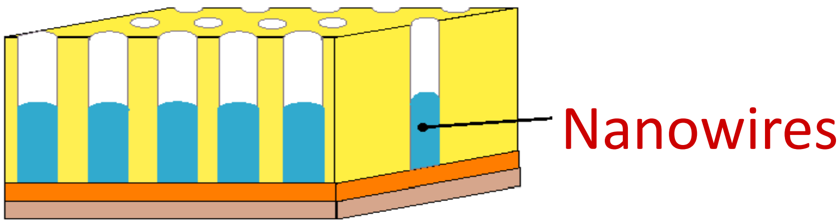


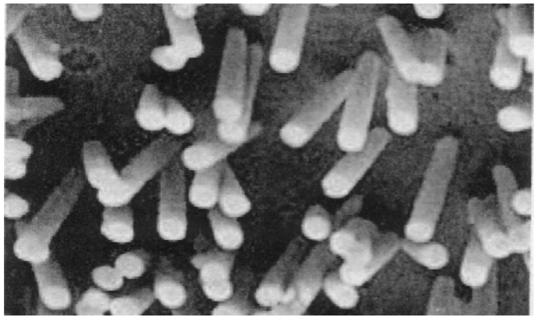
Array of 10 x 10 Cu clusters at $E_{substrate}$ = +10 mV vs. Cu/Cu^{2+}.

The same surface area after complete dissolution of the clusters at $E_{substrate}$ = +300 mV.

Kolb et al, 1998

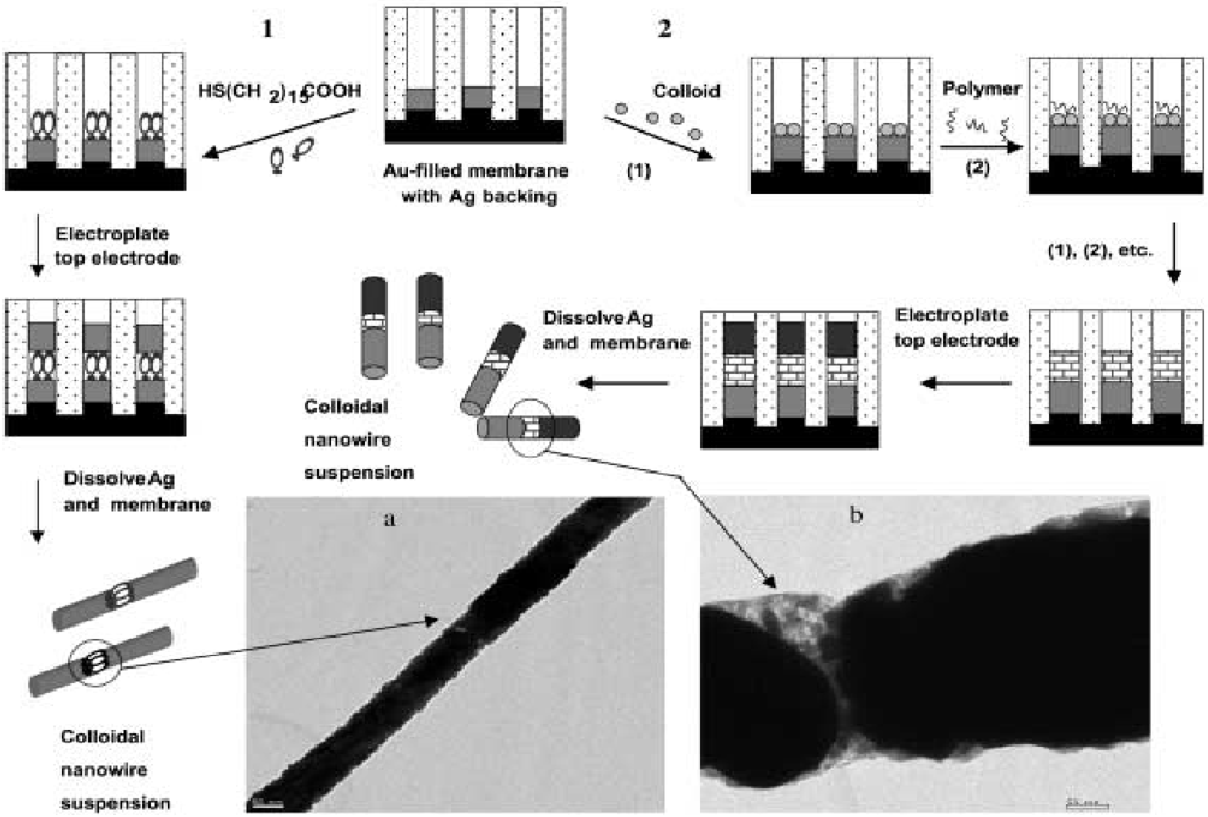
Template Methods: *Negative*





- **The beginning:** Possion used etched ion tracks in mica sheets as templates to fabricate metal wires. *P. E. Possion, Rev. Sci. Instrum. 41, 772* ***(1970)***.
- **The templates:** Ions tracks in mica or polycarbonate membranes, anodized alumina, phase segregated copolymer films are the popular choices.

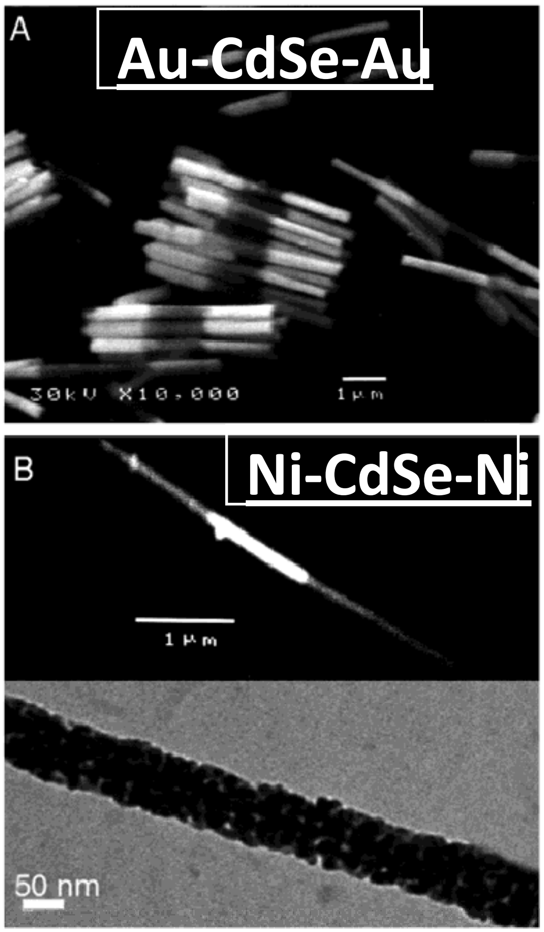
Building Block of Nanoelectronic Devices – *Molecular Junctions*

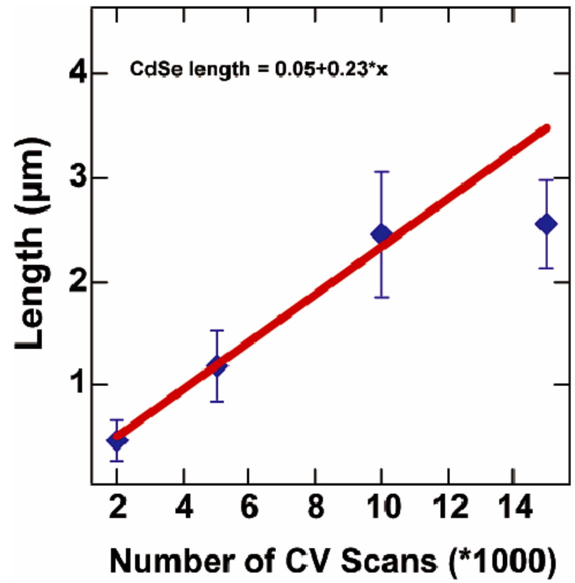


Top: Scheme for preparing nanowire devices by:1)self-assembly of a MHDA monolayer, or 2)layer-by-layer assembly of TiO_2 /PSS multilayer film on the exposed tip of a bottom metal electrode, followed by electroless seeding and electroplating of a top metal electrode.

Penn State Group

Building Block of Nanoelectronic Devices – *CdSe Nanojunctions*

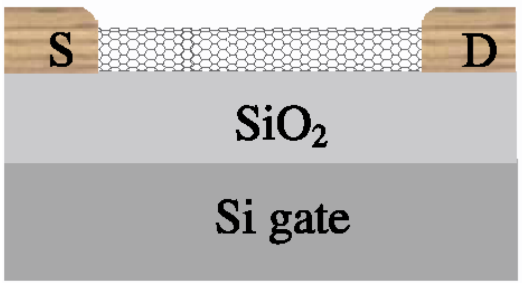


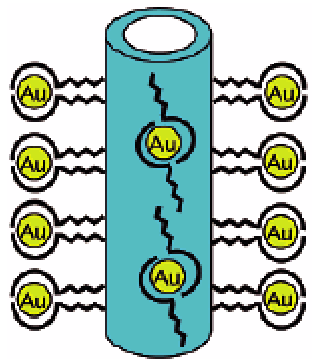


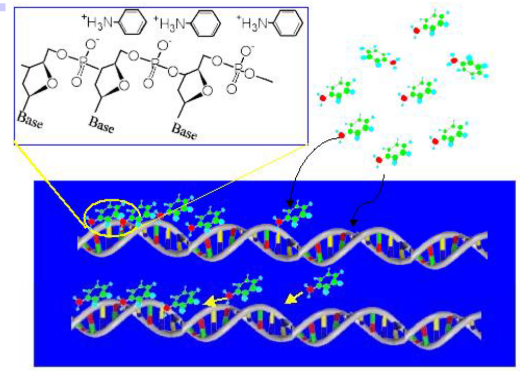
- Graph of CdSe segment length vs the number of cyclic voltammetric scans for 350-nm diameter nanowires. Error bars show the standard deviation in length.

J. Phys. Chem. 106, 7458(2002)

Positive Templates



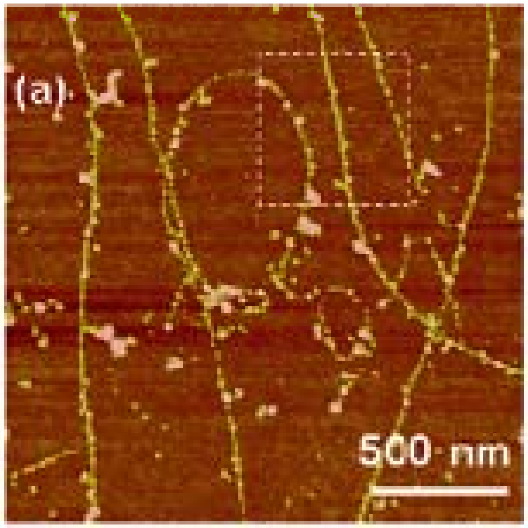


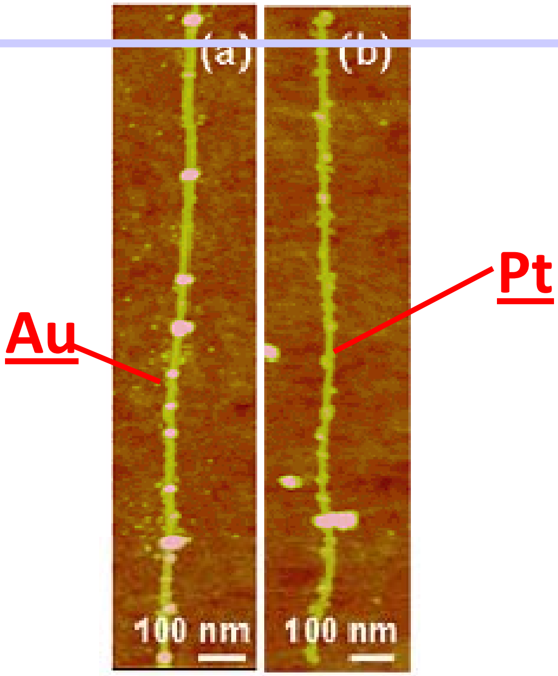


- Positive template method uses wire-like nanostructures, such as DNA and carbon nanotubes, as templates, and nanowires are formed on the outer surface of the templates.

- Unlike negative templates, the diameters of the nanowires are not restricted by the template sizes and can be controlled by adjusting the amount of materials deposited on the templates.

Carbon Nanotube Template

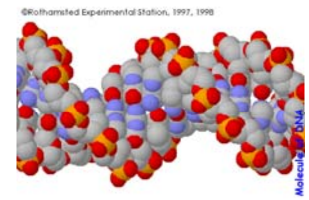


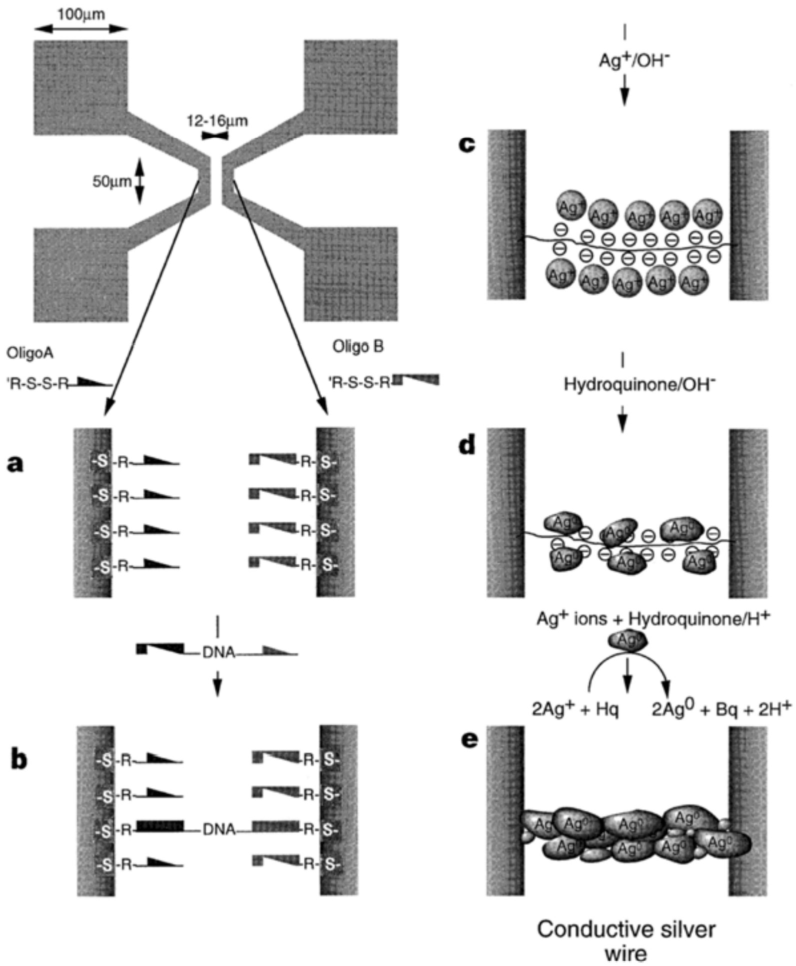


- After Pt or Au deposition on SWNTs, the sample was annealed at 600°C in air for 10 min, which leads to Pt/Au nanoparticles forming chain-like structures.
- In contrast to ordinary electroless deposition, no reducing agents are needed for SWNTs.

Dai et al JACS 124(31)9058, 2002.

DNA Template

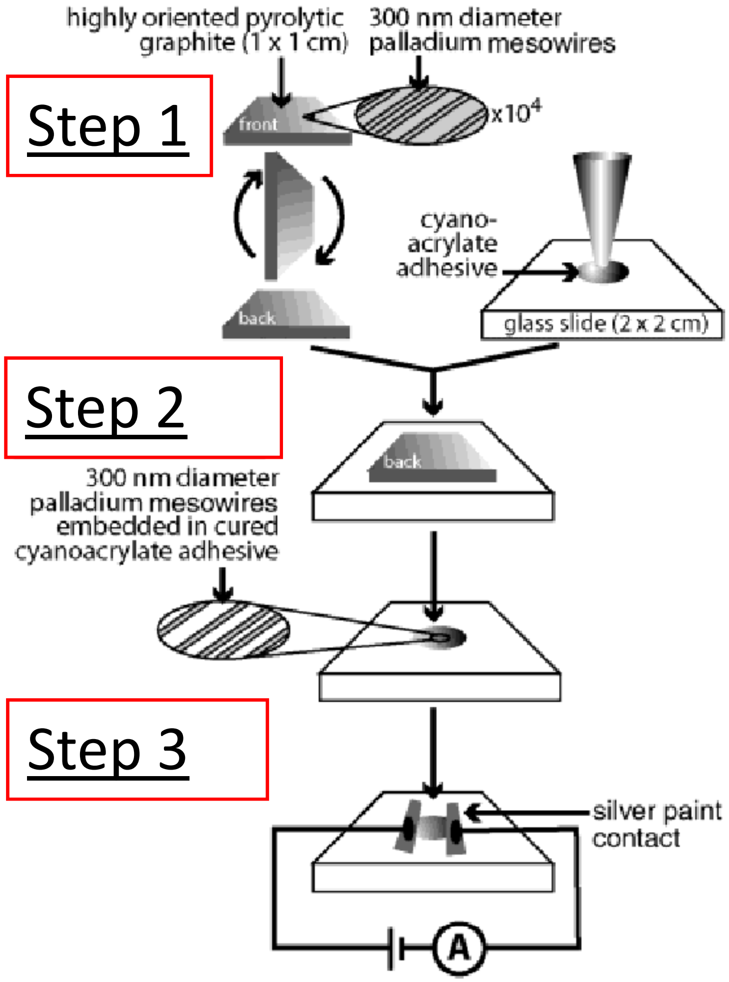




- The first step is to fix a DNA strand between two electrical contacts.
- The DNA is then exposed to a solution containing Ag^+ ions. The Ag^+ ions bind to DNA and are then reduced by a basic hydroquinone solution to form Ag nanoparticles decorating along the DNA chain.
- The nanoparticles are further 'developed' into a nanowire using a photographic enhancement technique.

Braun, E. et al. Nature 391, 775, 1998

Graphite Step Edge Template



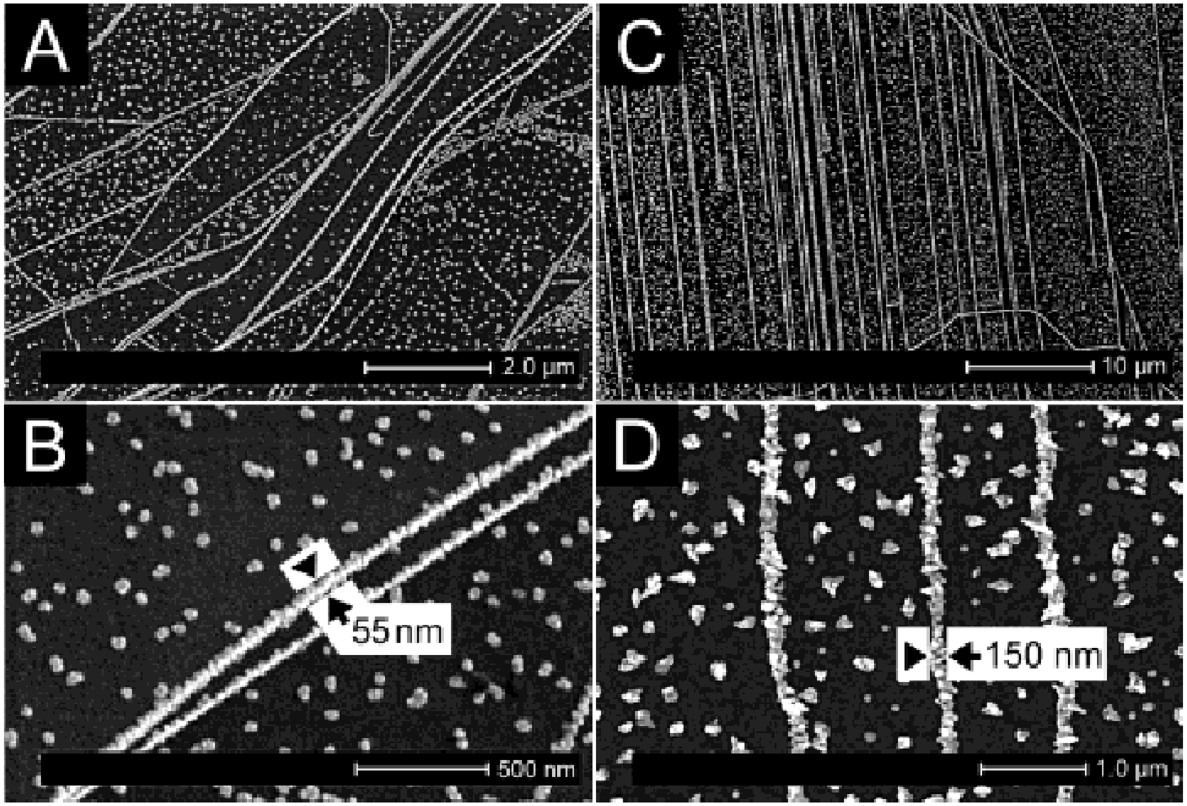
Step 1: Electrodeposit Pd nanowires.

Step 2: Transfer the Pd wires to a glass slide.

Step 3: Apply silver contacts.

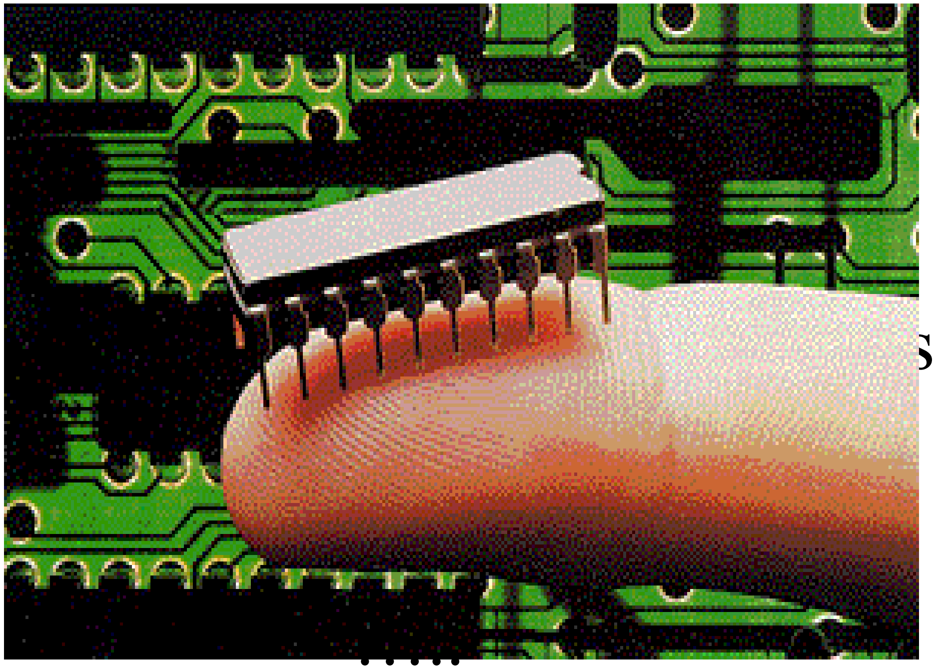
Penner et al.

Graphite Step Edge Template



Penner et al.

Applications



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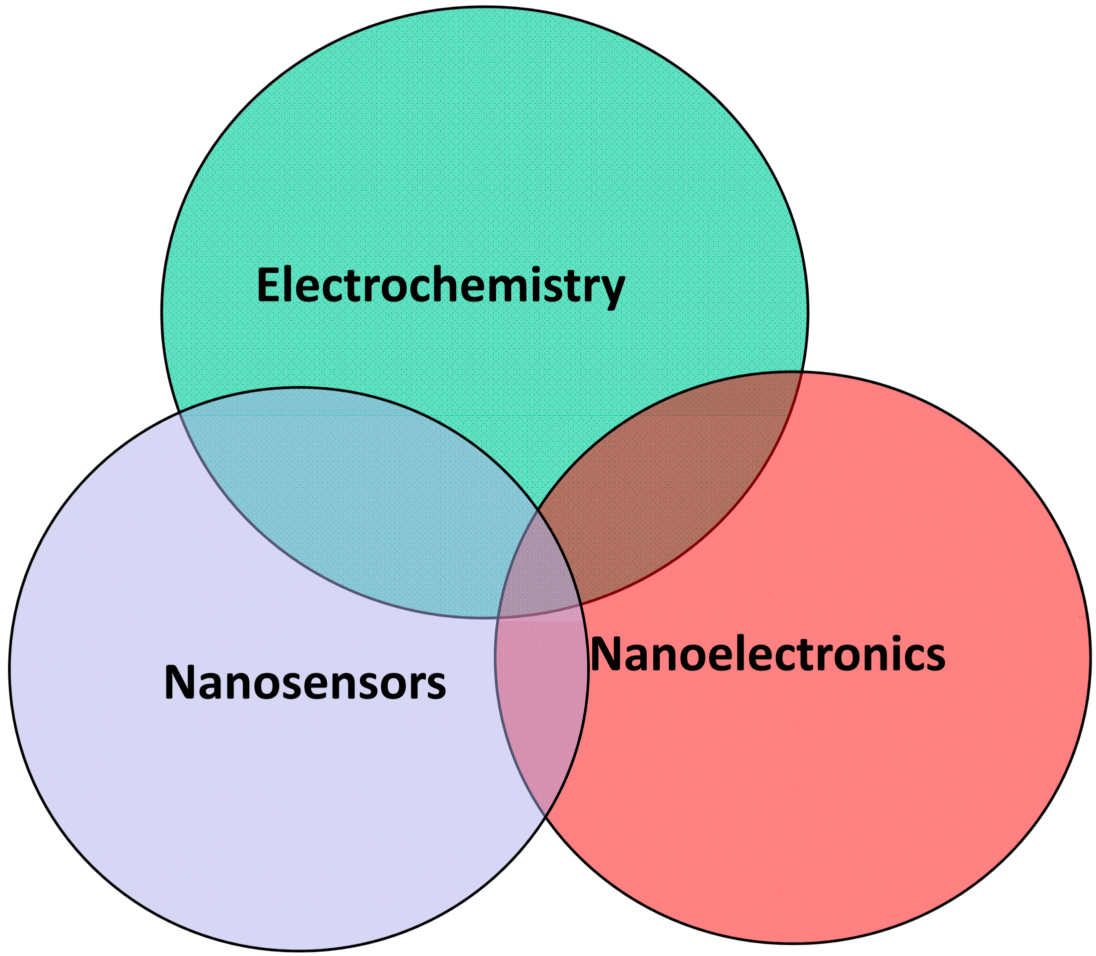
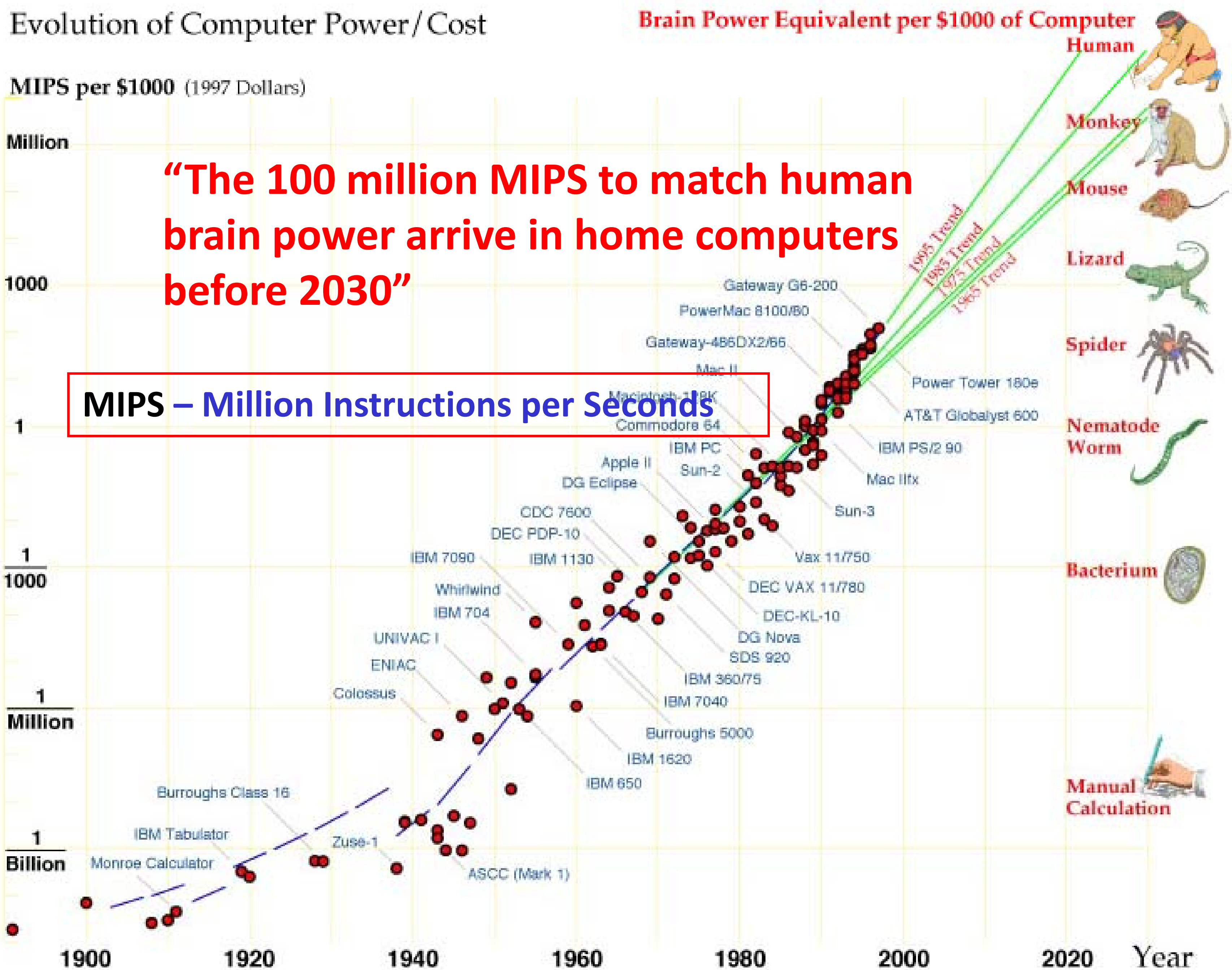

Electrochemistry
Nanosensors
Nanoelectronics



"The 100 million MIPS to match human brain power arrive in home computers before 2030"

MIPS – Million Instructions per Seconds

Nanoelectronics

- **Electronics based on new phenomena occurring at Nano-scale**

Single Electron Transistor

Ballistic transport

Kondo effect

Electron tunneling

Spintronics

Molecular Electronics

Localization

Nanosensors

Nanosensors

Nanosensors are any biological, chemical, or surgical sensory points used to convey information about nanoparticles to the macroscopic world. Their use mainly include various medicinal purposes and as gateways to building other nanoproducts, such as computer chips that work at the nanoscale and nanorobots. Presently, there are several ways proposed to make nanosensors, including top-down lithography, bottom-up assembly, and molecular self-assembly

Sensor

- A sensor is an instrument that responds to a physical stimulus (such as heat, light, sound, pressure, magnetism, or motion)

- It collects and measures data regarding some property of a phenomenon, object, or material

- Sensors are an important part to any measurement and automation application

- The sensor is responsible for converting some type of physical phenomenon into a quantity measurable by a data acquisition (DAQ) system

Why Nanosensors

- Particles that are smaller than the characteristic lengths associated with the specific phenomena often display new chemistry and new physics that lead to new properties that depend on size

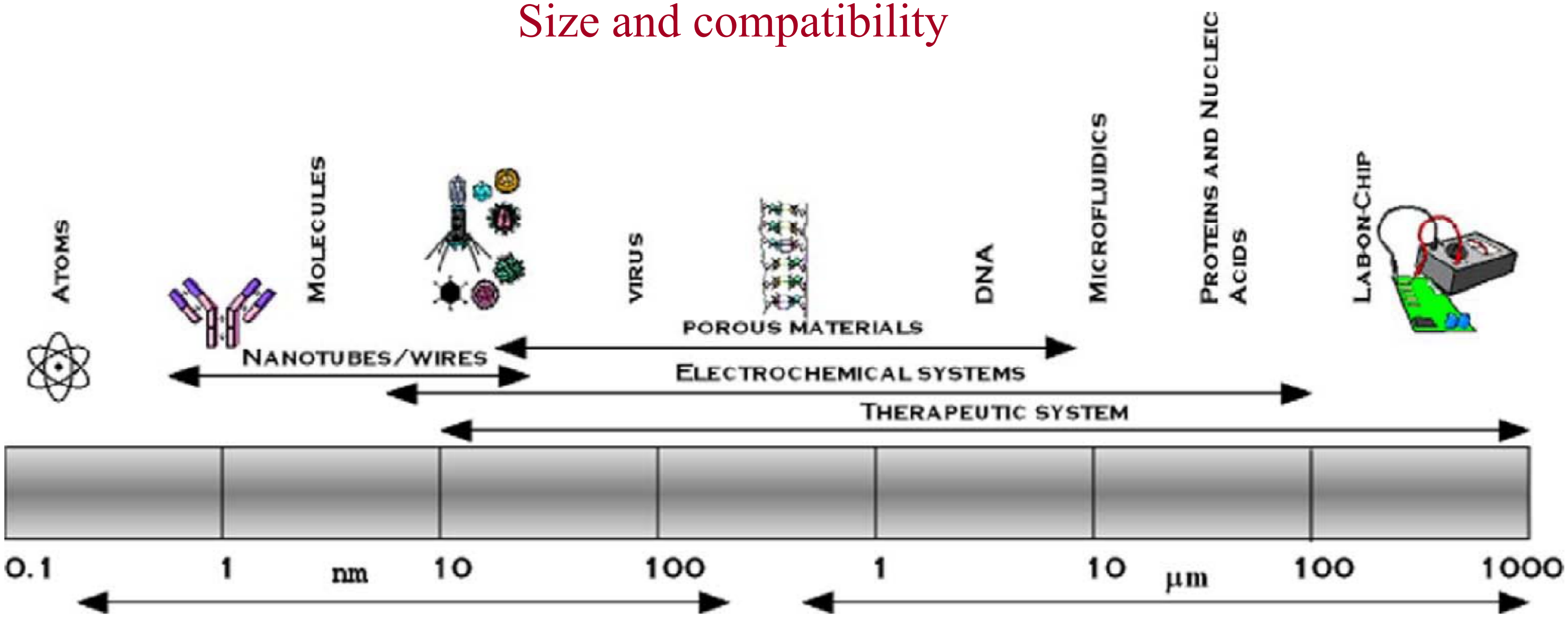
- When the size of the structure is decreased, surface to volume ratio increases considerably and the surface phenomena predominate over the chemistry and physics in the bulk

- The reduction in the size of the sensing part and/or the transducer in a sensor is important in order to better miniaturise the devices

- Science of nano materials deals with new phenomena, and new sensor devices are being built that take advantage of these phenomena

- Sensitivity can increase due to better conduction properties, the limits of detection can be lower, very small quantities of samples can be analysed, direct detection is possible without using labels, and some reagents can be eliminated.

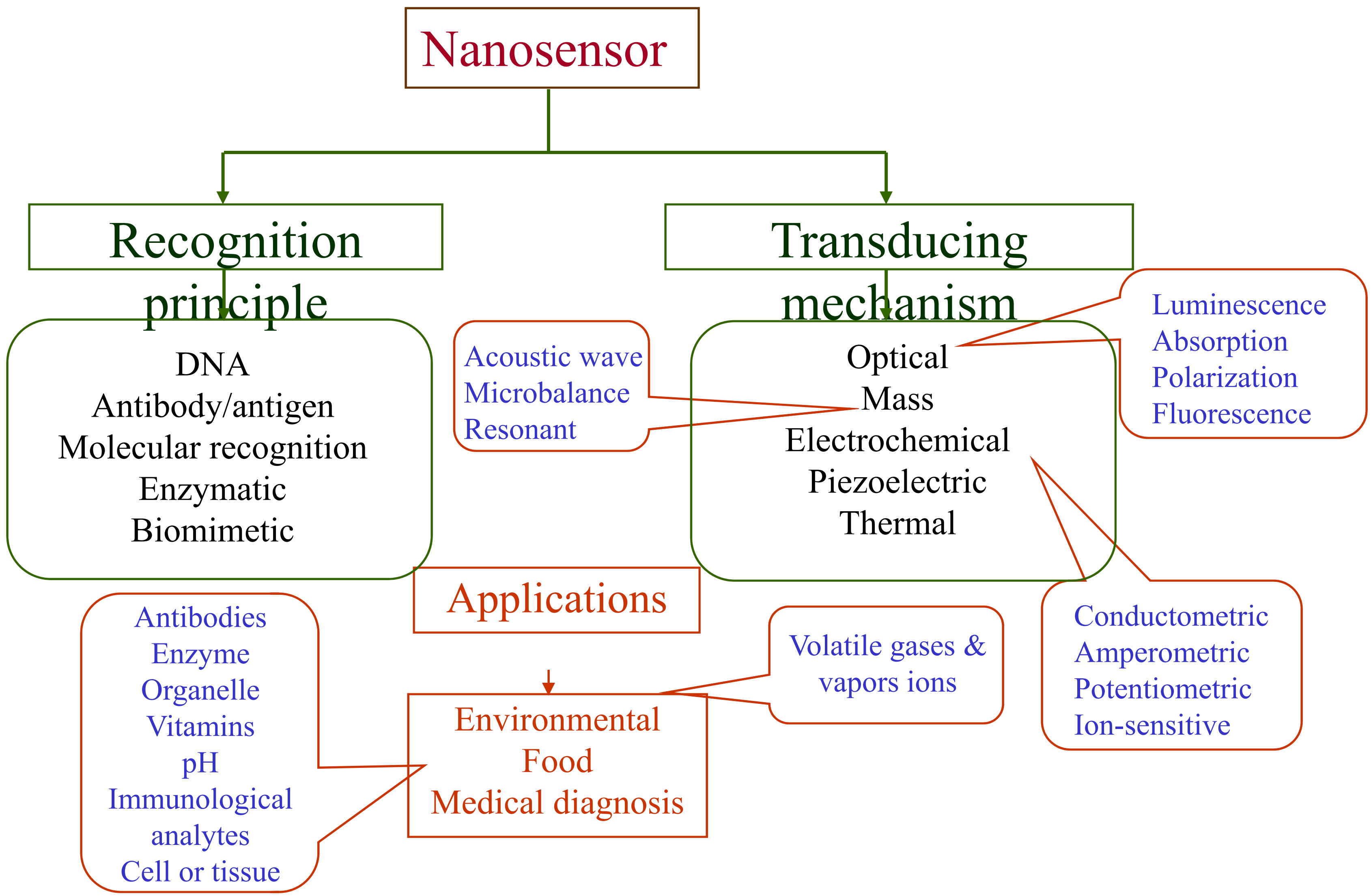
Size and compatibility



Nano sensors deliver real-time information about the antibodies to antigens, cell receptors to their glands, and DNA and RNA to nucleic acid with a complimentary sequence

Sensitivity of the conventional biosensors is in the range between 10^3 and 10^4 colony forming units (CFU)/ml. The dimensional compatibility of nanostructured materials renders nanotechnology as an obvious choice derived from its ability to detect ~ 1 CFU/ml sensitivity

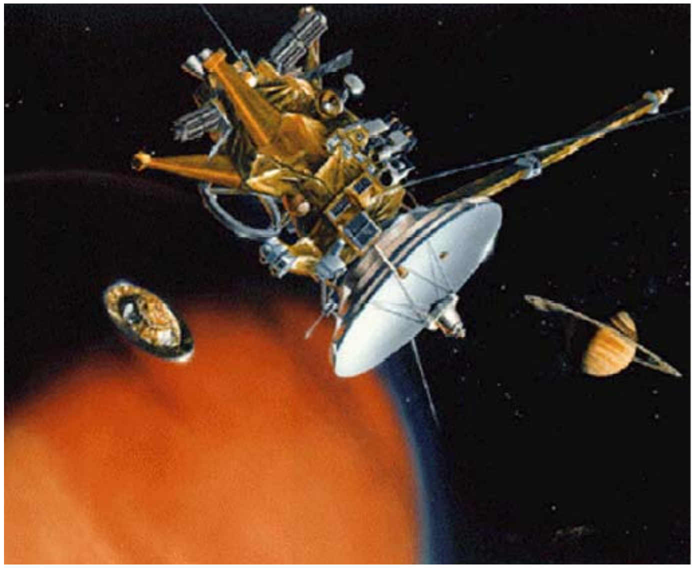
Reduced detection time than conventional methods



Scheme 1. Representation of recognition process and application of Nanosensor

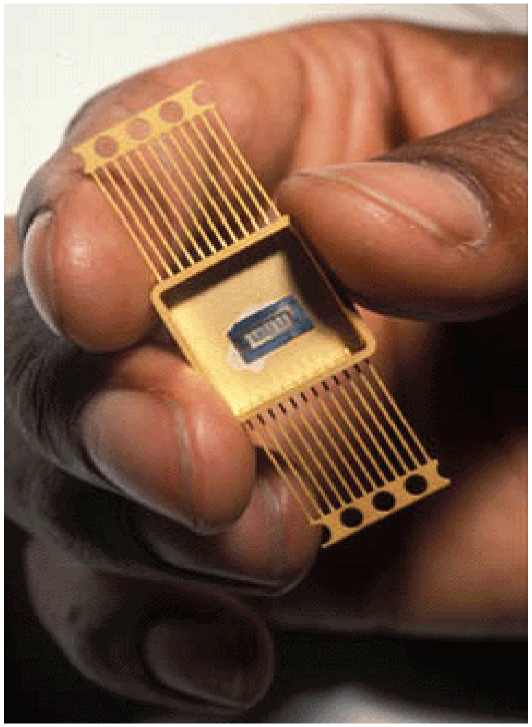
Outline

- Definition of Nanosensors
- Current Nanosensor Devices
  - Nanostructured materials - e.g. Porous Silicon
  - Nanoparticles
  - Nanoprobes
  - Nanowire/nanotube Nanosensors
  - Nanosystems – e.g. cantilevers, NEMS
- Applications of Nanosensors
- Conclusions
- Questions



Definition of Nanosensors

- Nanosensor: an extremely small device capable of detecting and responding to physical stimuli with dimensions on the order of one billionth of a meter
- Physical Stimuli: biological and chemical substances, displacement, motion, force, mass, acoustic, thermal, and electromagnetic

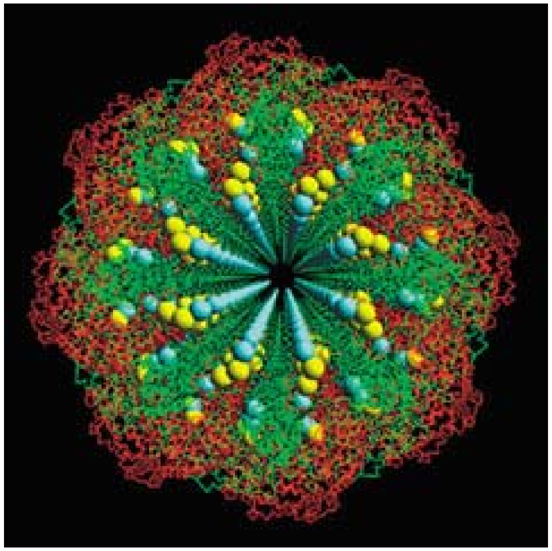


http://www.rpi.edu/locker/25/001225/public_html/nanowebprojects/laurasmith/nanosensors.ppt

Definition of Nanosensors (cont.)

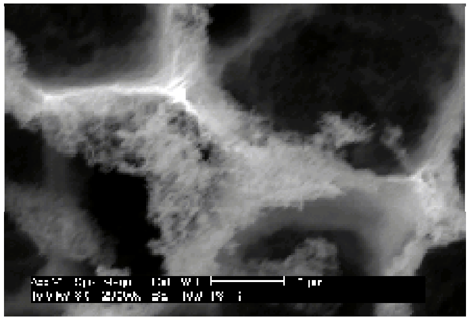
Current nanosensors device:

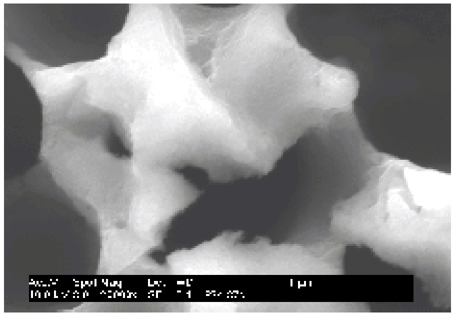
- Nanostructured materials - e.g. porous silicon
- Nanoparticles
- Nanoprobes
- Nanowire nanosensors
- Nanosystems
  - Cantilevers, NEMS, mostly theoretical

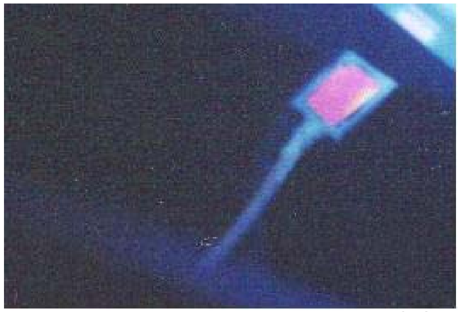


Porous Silicon

- Description: Porous silicon is identical to the silicon used in many technological applications today, but its surface contains tiny pores ranging from < 2nm to microns, that can absorb and emit light.
- History:
  - Material first reported in 1956 by Uhlir as an effect from electrochemical polishing studies using a low current density.
  - Chemical etching with HF/HNO3 also produced porous silicon.
  - Crystalline etch channels found in early 1970’s by Theunissen.
  - Pickering et. al. first noted photoluminescence at room temperature.
  - Canham observed room temperature fluorescence in 1990 and suggested Quantum Confinement as origin of fluorescence.

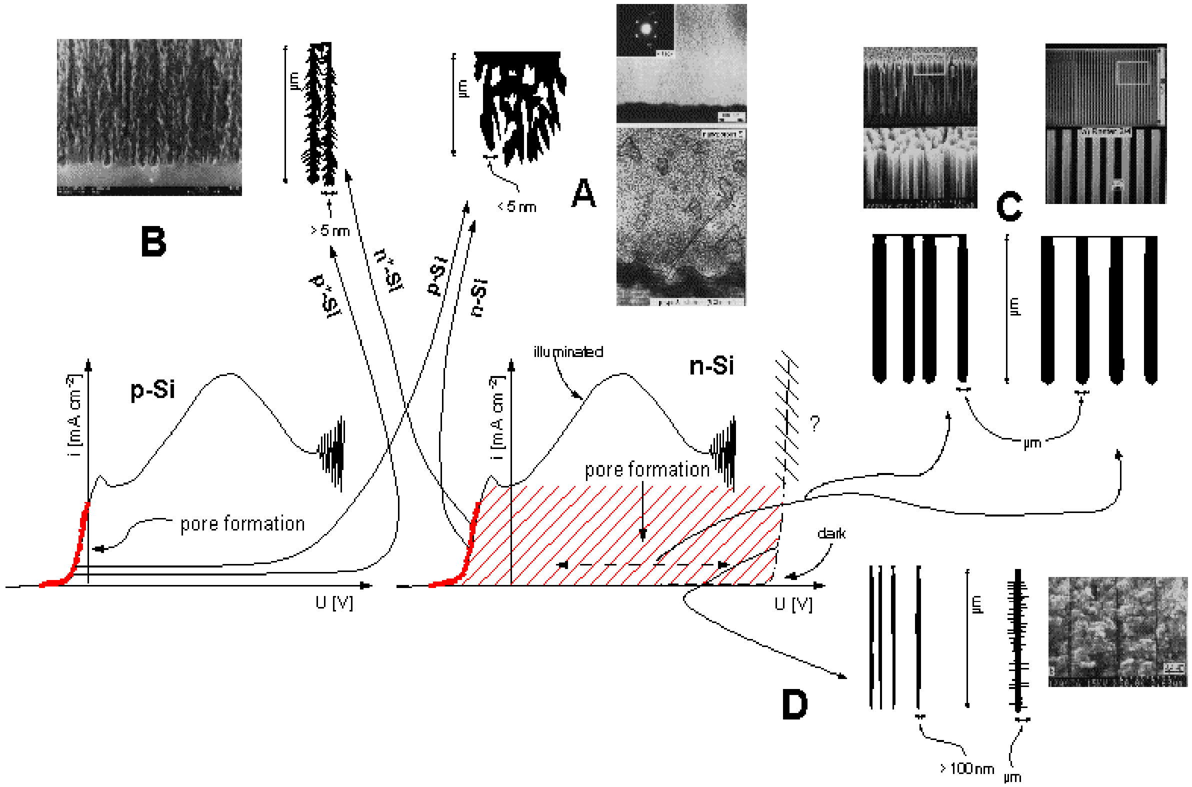






http://216.239.39.100/search?q=cache:iE0mYxRdrn0J:mhegazy.topcities.com/Porous_Silicon.PDF+&hl=en&ie=UTF-8

Porous Silicon



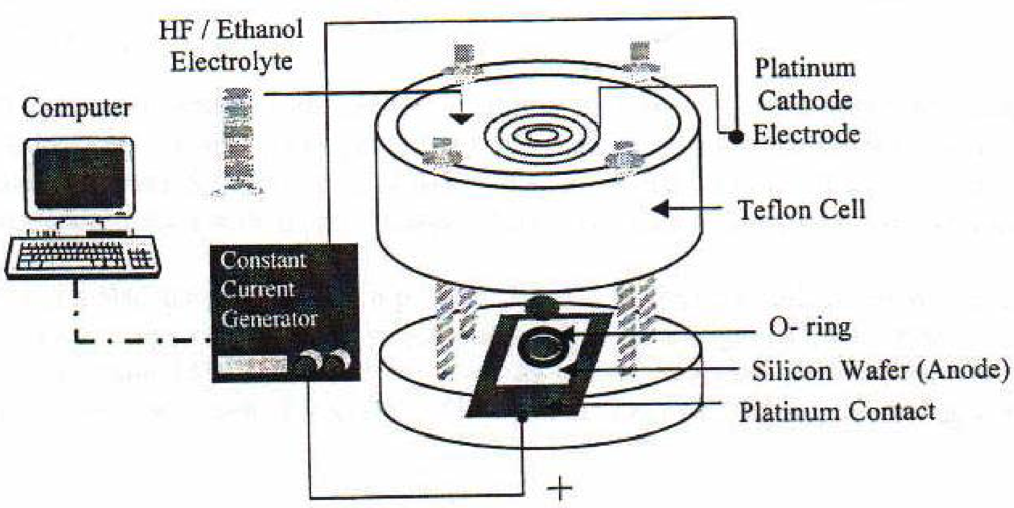
Classification of porous silicon

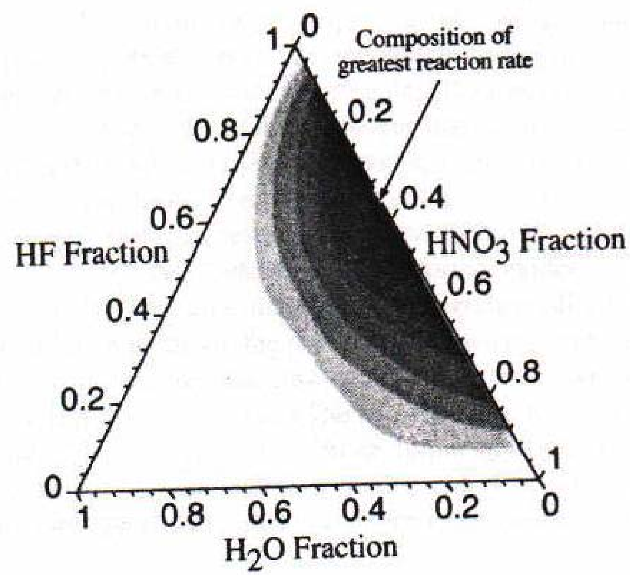
- **A: Nanoporous silicon - (features < 5nm)**
- **B: Mesoporous silicon - (features 5nm - 100nm)**
- **C: Macroporous silicon - (features > 100nm)**
- **D: Pores generated by electrical breakdown**

http://www.tf.uni-kiel.de/matwis/amat/poren/poreover.html

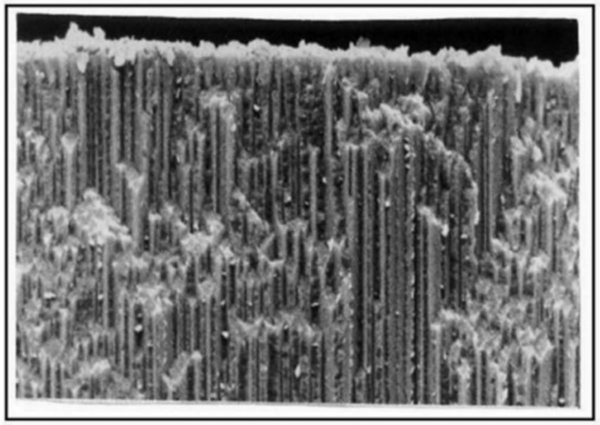
Porous Silicon

- Manufacturing Methods
  - Electrochemical Etching
  - Chemical Etching
  - Spark Erosion
  - Chemical Vapor Deposition

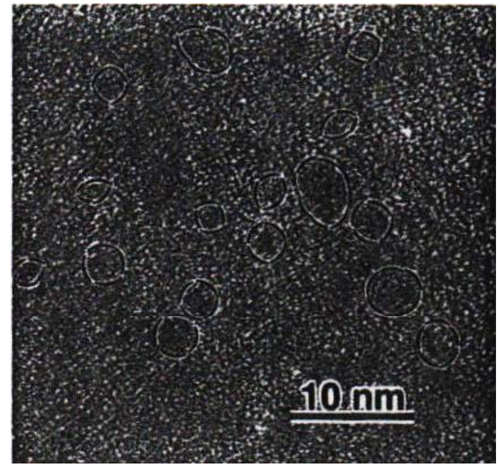


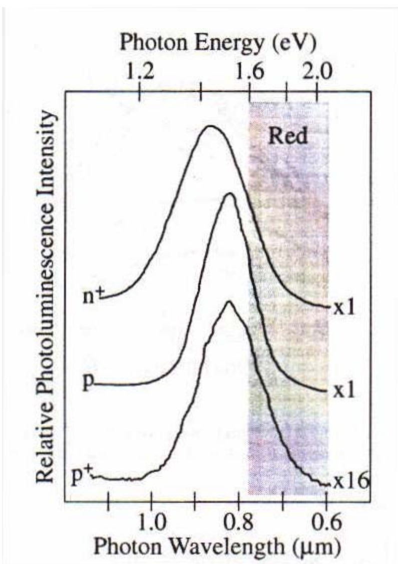


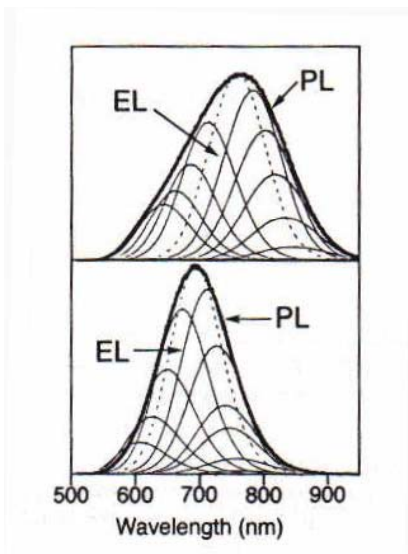
Porous Silicon



Micrograph of electro-etched porous silicon surface (from Sailor)





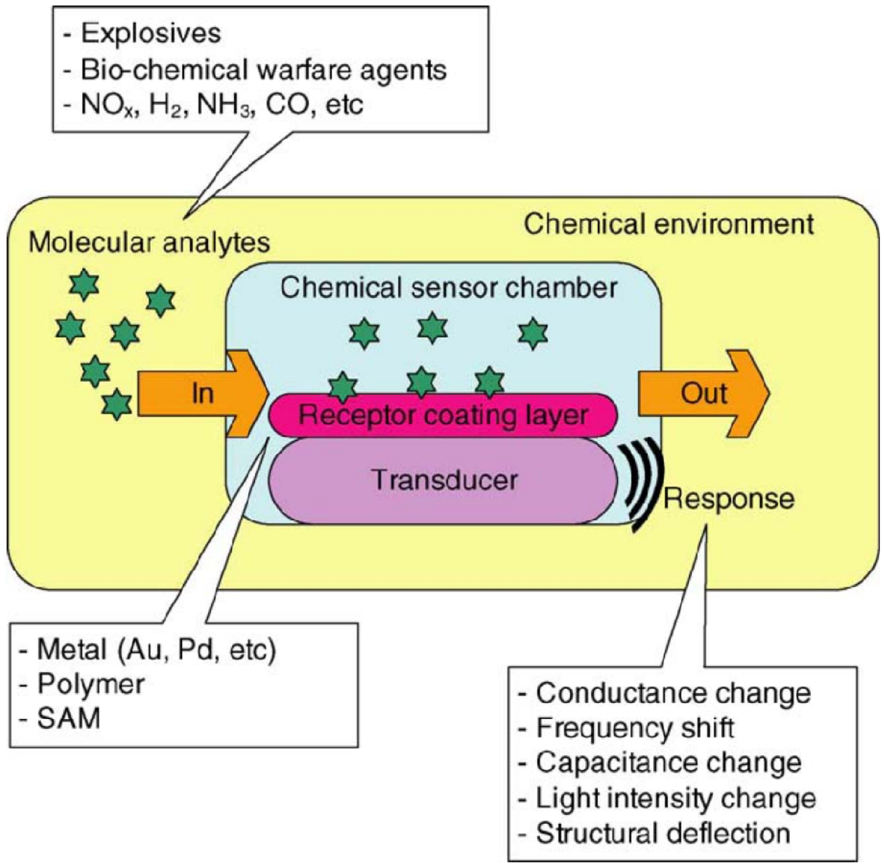


Properties

- Porosity
- Photoluminescence
- Electroluminescence
- Reflectivity
- Conduction

Electronic Nose

General structure of a chemical sensor



Three figures of merit related to gas sensing technology:

- Reversibility
- Sensitivity
- Selectivity

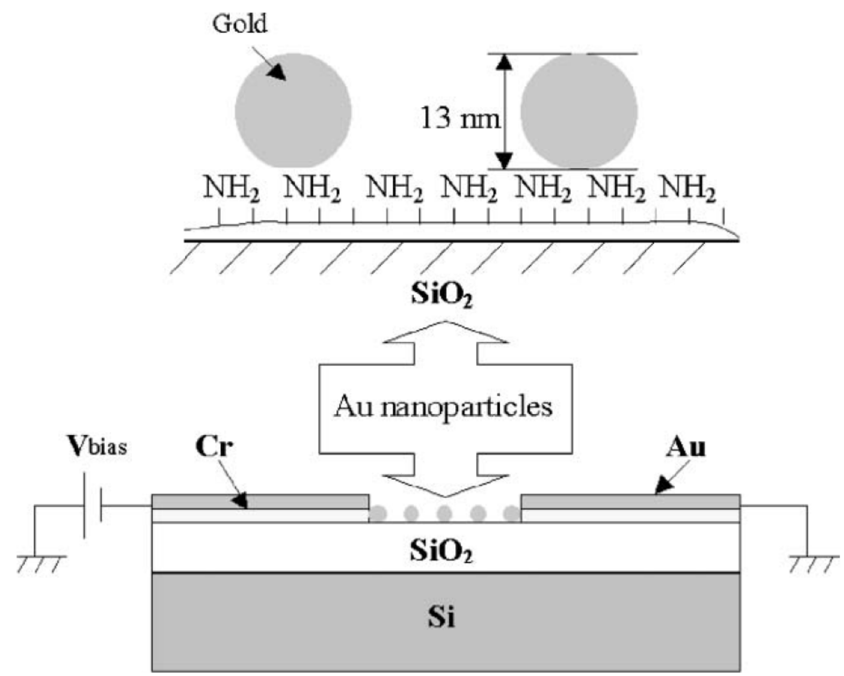
H_2S nanosensor

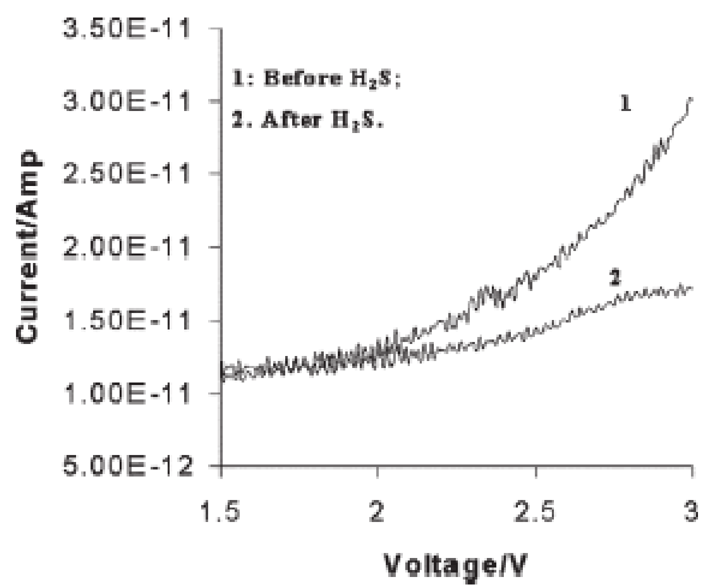
- In each sensing cell, two electrodes, source and drain, are made to have a nanoscale gap between them

- A typical gap-width of ca. 40–60 nm has been achieved

- Au nanoparticles are placed randomly
over the gap area

- Adsorption of H_2S molecules onto the nanoparticles may significantly change the hopping behaviour of electrons through the particles





Measurement of the I–V curves before and after the H_2S exposure
(3 minutes exposure, pure H_2S gas, at room temperature)

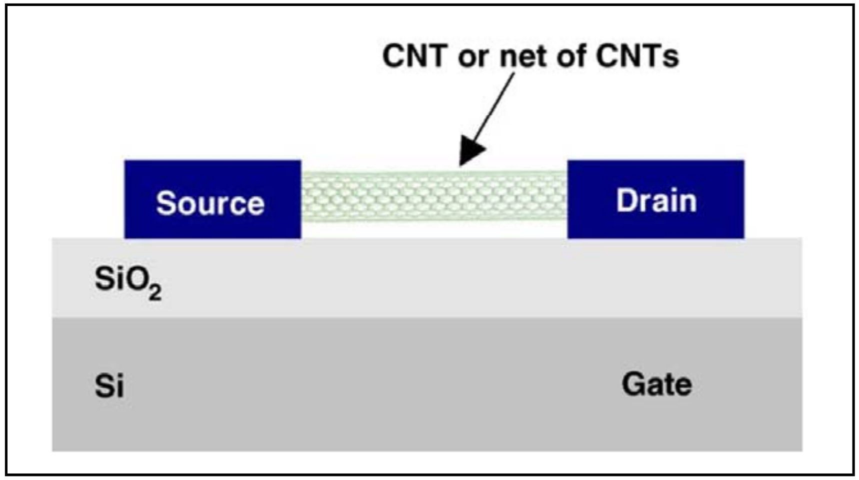
Exceptional properties of carbon nanotubes

- ✓ CNT have a high length-to-radius ratio, which allows for greater control over the unidirectional properties of the materials produced

- ✓ they can behave as metallic, semiconducting or insulating material depending on their diameter, their chirality, and any functionalisation or doping

- ✓ they have a high degree of mechanical strength. In fact they have a greater mechanical strength and flexibility than carbon fibres

- ✓ their properties can be altered by encapsulating metals inside them to make electrical or magnetic nanocables or even gases, thus making them suitable for storing hydrogen or separating gases



Schematic structure of a Carbon Nanotube-FET

- Electrical properties of CNT are sensitive to the effects of charge transfer and chemical doping by various molecules

- The electronic structures of target molecules near the semiconducting nanotubes cause measurable changes to the nanotubes' electrical conductivity

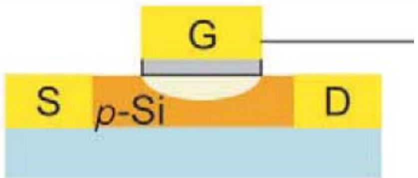
- Nanosensors based on changes in electrical conductance are highly sensitive but they are also limited by factors such as their inability to identify analytes with low adsorption energies, poor diffusion kinetics and poor charge transfer with CNTs

CNT based Nano Sensors

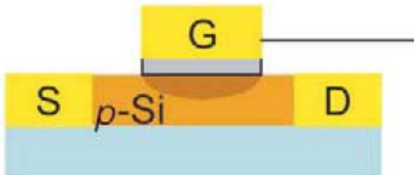
System	Target species	Salient feature	Reference
Single wall nanotubes (SWNT)	NH_3 and NO_2	Sensitive to 200 ppm of NO_2, and 1% of NH_3.	*Science* 287 **(2000) 1801.**
Single wall nanotubes (SWNT)	N_2, He, O_2, and Ar	Gas concentrations as low as 100 ppm can be detected	*Appl. Phys. Lett.* 83 **(2003) 2280.**
Multi-wall carbon nanotubes (MWCNTs)	NH_3	Gas concentrations as low as 10 ppm can be detected. The sensor showed a reversible response of few minutes.	*J. Phys. D: Appl. Phys.* 36 **(2003) L109.**
Poly(*o*-anisidine) (POAS) coated CNT	HCl	Nine times increase in sensitivity compared to uncoated CNT	*Chemical Physics Letters, Volume 383(5-6) (2004) 617.*
MWNT-SiO_2	CO_2, O_2 and NH_3	Sensor response time is approximately 45 s, 4 min, and 2 min for CO_2,O_2, and NH_3, respectively. The sensor response is reversible for O_2 and CO_2 , but irreversible for NH_3	*IEEE Sens*. J. 2 (2002) 82.
Single-walled carbon nanotube (SWNT)	β-D-glucose	Senses β-D-glucose in solution phase by two distinct mechanisms of signal transduction: fluorescence and charge transfer.	*Nat. Mater*. 4 (2005) 86.
Poly(vinylferrocene) (PVF) derivatised MWCNTs	Glucose	Glucose concentration in real blood sample can be determined.	*The Analyst* 131 (2006) 670.

Field-Effect Sensors (FET)

Si nanowire sensor device

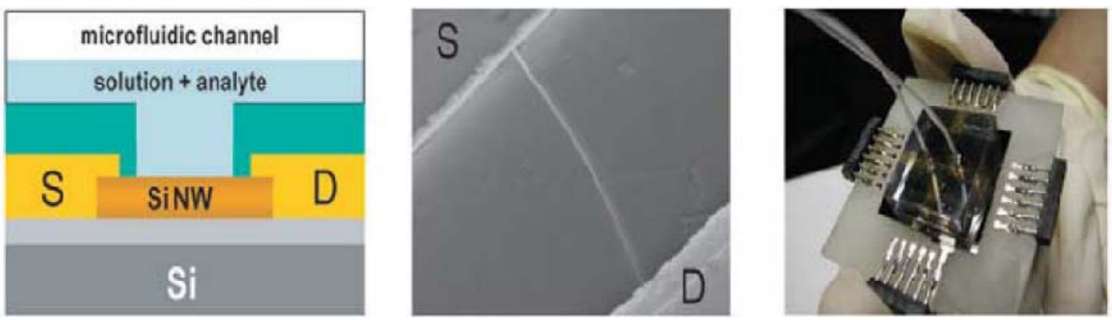


$V_G > 0$ depletion of carriers conductance decreases

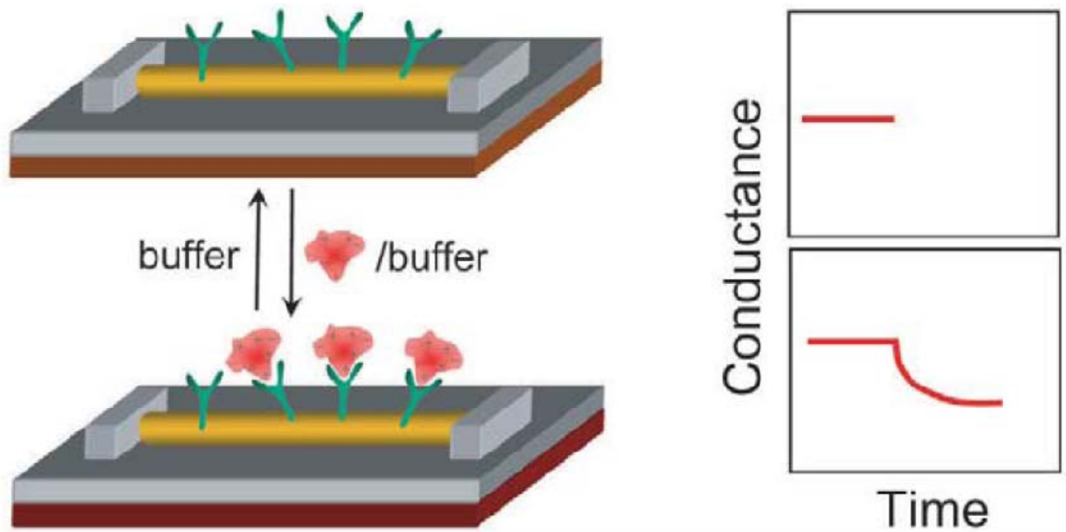


$V_G < 0$ accumulation of carriers conductance increases

Schematic of a regular planar FET device, where S, D, & G correspond to source, drain, and gate, respectively



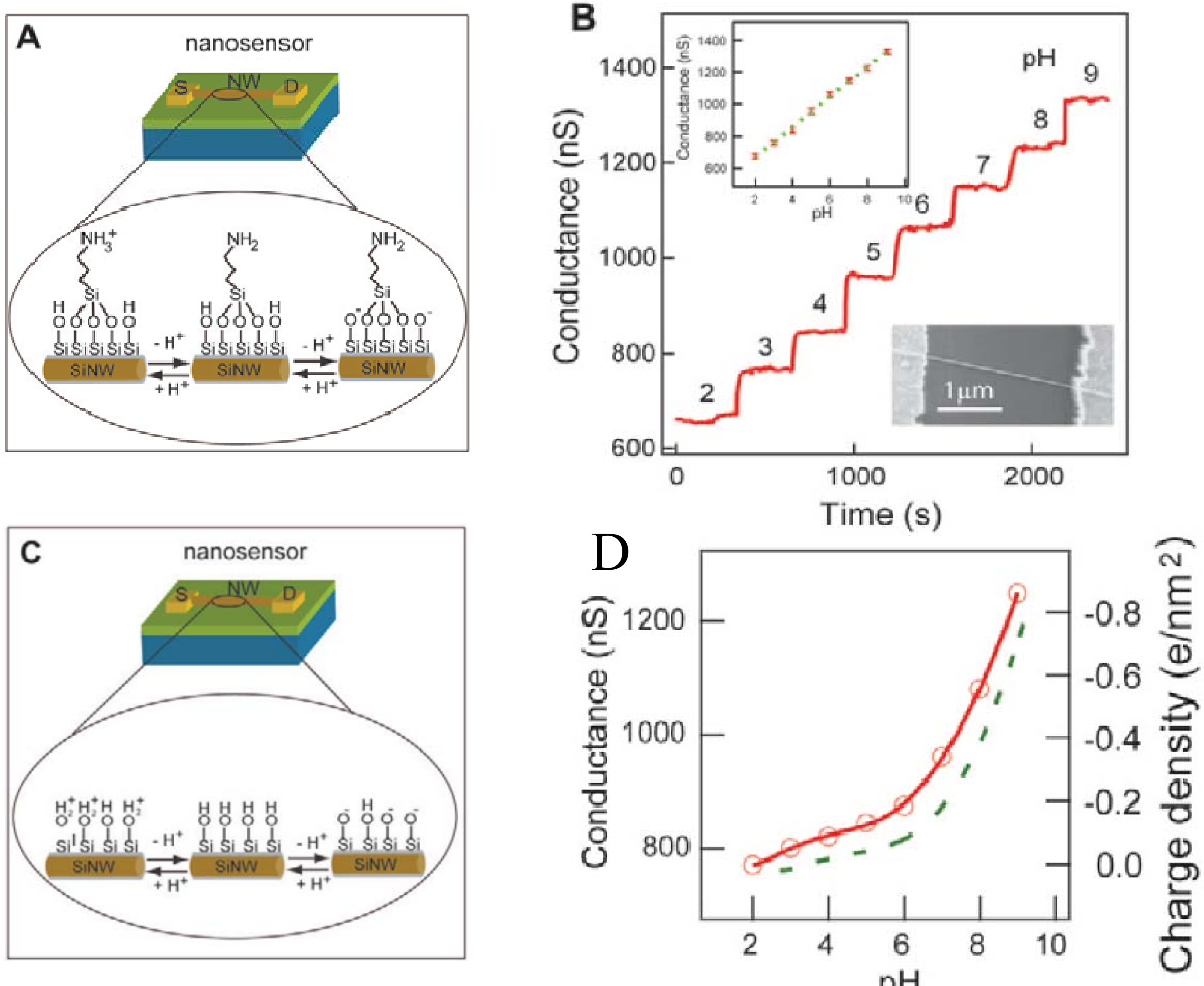
Cross-sectional diagram and scanning electron microscopy image of a single Si nanowire sensor device, and a photograph of a prototype nanowire sensor biochip with integrated microfluidic sample delivery.



Schematic of a Si nanowire-based FET device configured as a sensor with antibody receptors (green), where binding of a protein with net positive charge (red) yields a decrease in the conductance

- A general sensing device can be configured as illustrated in Fig. 1C, where specific sensing is achieved by linking a recognition group to the surface of the nanowire
- Si nanowires with their natural oxide coating make this receptor linkage straightforward
- When the sensor device with surface receptor is exposed to a solution containing a macromolecule like a protein that has a net positive charge in aqueous solution, specific binding will lead to an increase in the surface positive charge and a decrease in conductance for a p-type nanowire device

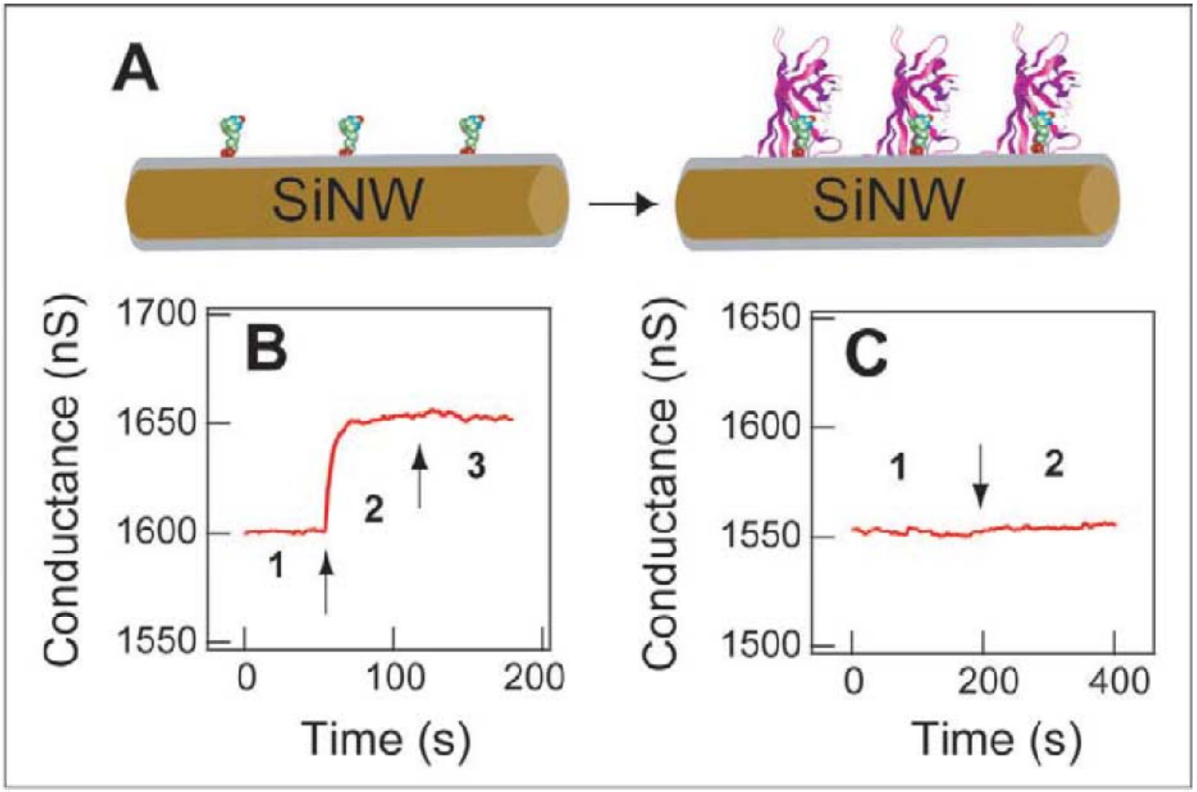
Nanowire pH sensors



(A) Schematic of an amino-functionalized nanowire device. (B) Changes in nanowire conductance as the pH of solutions delivered to the sensor is varied from 2 to 9; inset is a plot of conductance data versus pH. (C) Schematic of an unmodified nanowire sensor containing silanol groups. (D) Conductance of an unmodified Si nanowire device (red) versus pH.

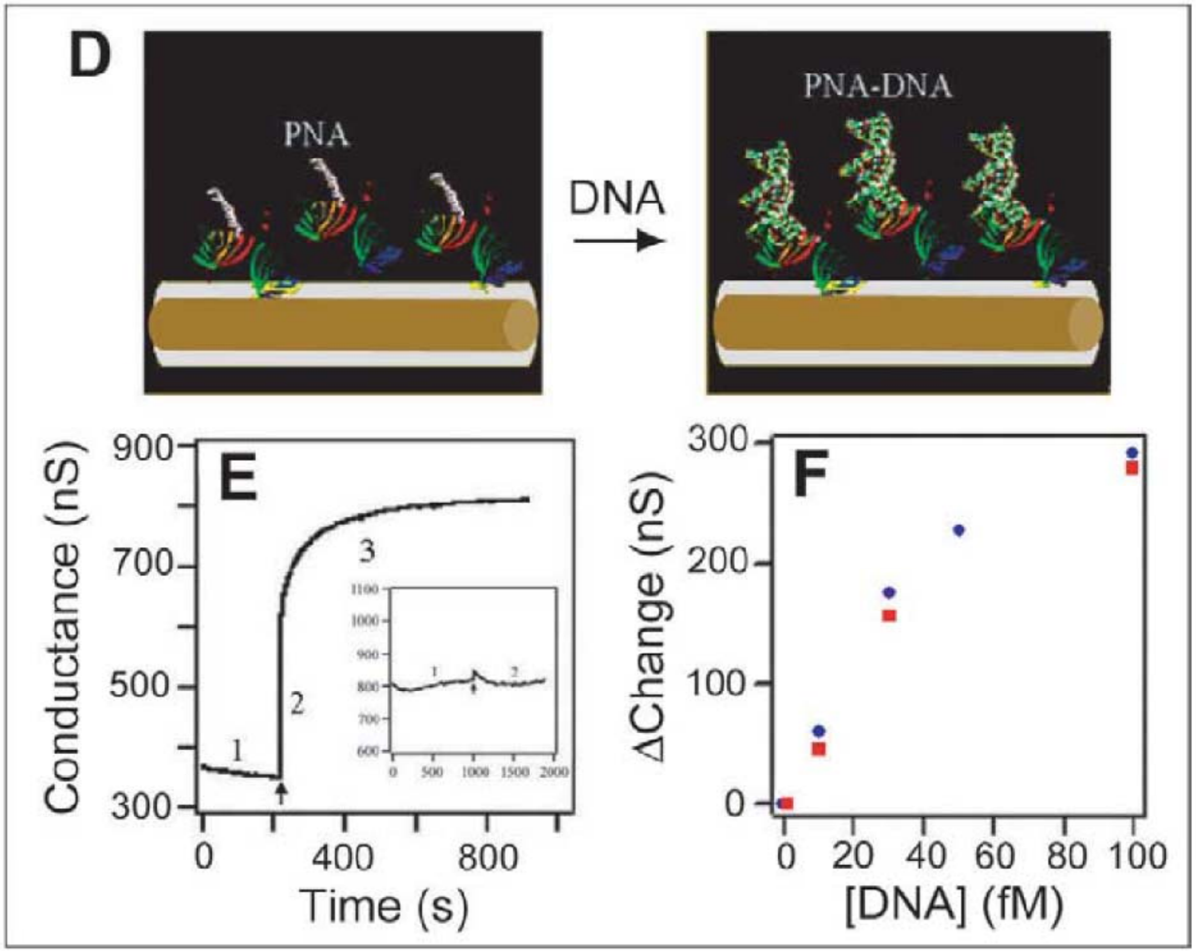
Real-time detection of proteins and DNA

Detection of Proteins



(A) Schematic of a biotin-modified Si nanowire and subsequent binding of streptavidin to the modified surface. (B) Plot of conductance versus time for a biotin-modified Si nanowire, where region 1 corresponds to the buffer solution, region 2 corresponds to the addition of 250 nM streptavidin, and region 3 corresponds to pure buffer solution. (C) Conductance versus time for an unmodified Si nanowire, where regions 1 and 2 are the same as in (B).

Detection of DNA



(D) Schematic of a Si nanowire sensor surface modified with PNA receptor before and after duplex formation with target DNA. (E) Si nanowire DNA sensing where the arrow corresponds to the addition of a 60 fM complementary DNA sample and the inset shows the device conductance following addition of 100 fM mutant DNA. (F) Conductance versus DNA concentration, where data points shown in red and blue are obtained from two independent devices.

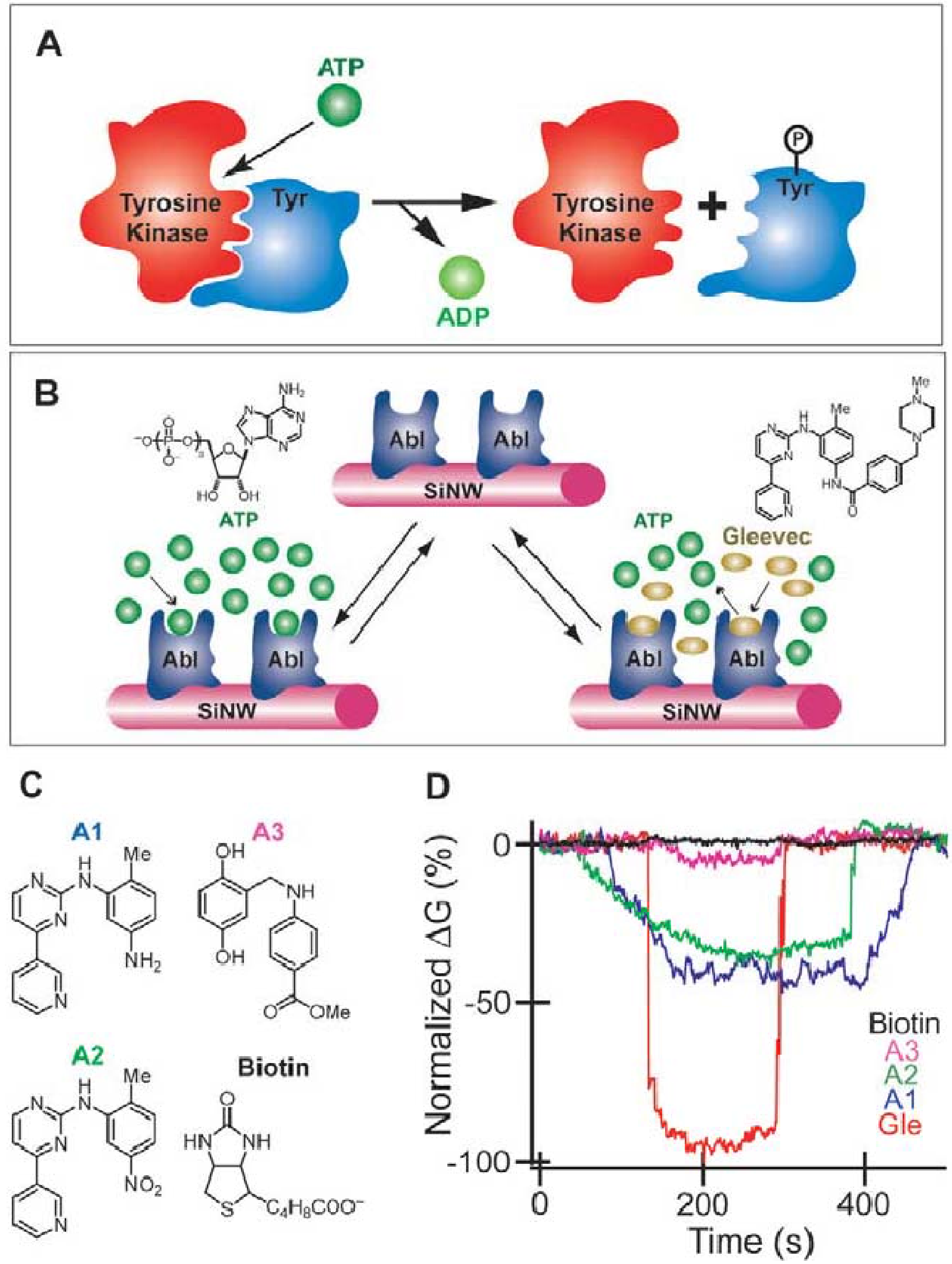
Nanosensors for drug discovery

(A) Illustration of tyrosine kinase function, where ATP binds to the kinase active site and then phosphate is transferred to a tyrosine (Tyr) residue of the substrate protein.

(B) Detection of ATP binding and small-molecule inhibition using a Si nanowire sensor device functionalized with the tyrosine kinase Abl.

(C) Structures of small molecules investigated for the inhibition of ATP binding to Abl.

(D) Normalized conductance versus time data recorded from Ablmodified Si nanowire devices using solutions containing 100 nM ATP and 50 nM small molecule Gleevec (red), A1 (blue), A2 (green), A3 (pink), and biotin (black).

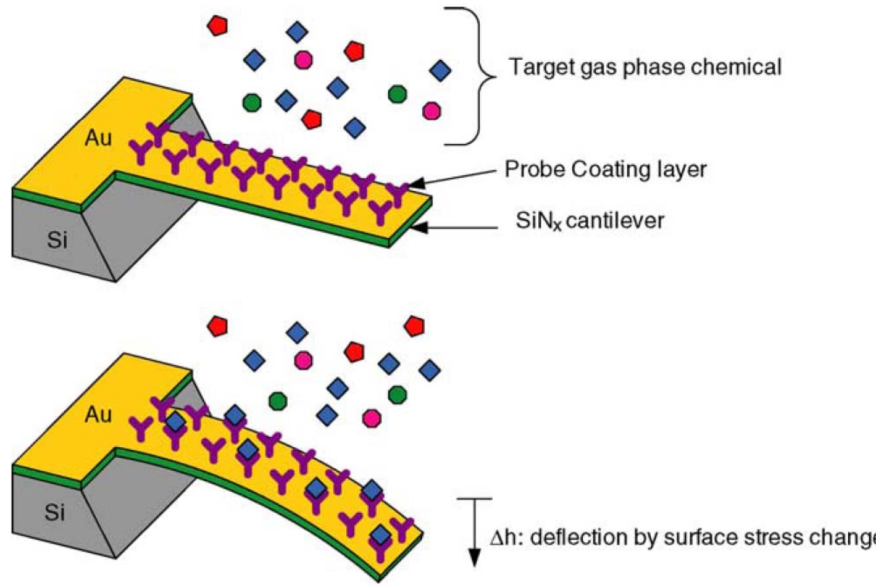


Cantilever sensors

➢ Chemical vapors at very low concentrations can be detected based on the surface stress changes generated by the interactions between probe and target molecules on their surfaces

➢ The magnitude of the surface stress change depends on the type of interaction taking place which includes

- Hydrogen bonding
- Electrostatic,
- van der Waals forces, etc.



Stoney's formula

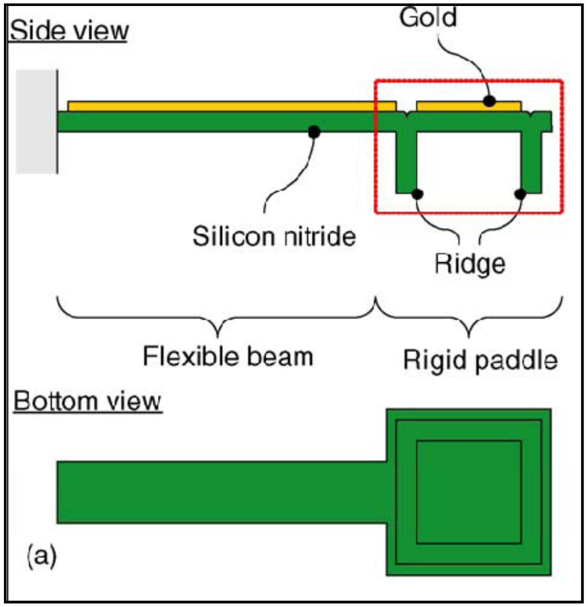
Surface stress change, $\Delta\sigma$, the deflection at the end of a cantilever, Δh, can be expressed as

Stoney's formula

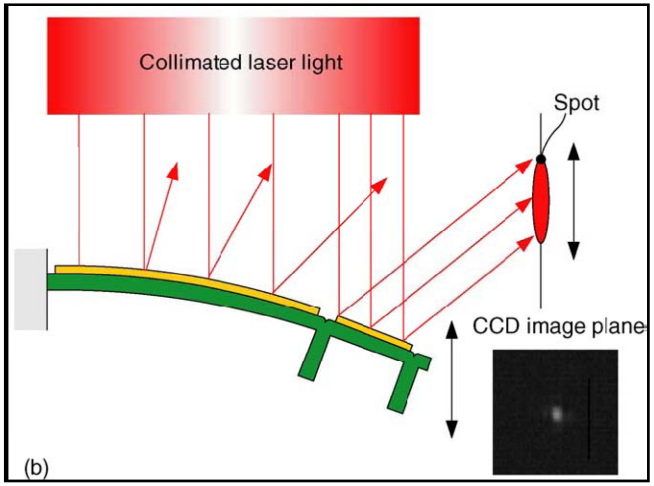
$$\Delta h = \frac{3(1-\nu)L^2}{Et^2} \cdot \Delta\sigma,$$

where L and t are length & thickness of the cantilever, respectively
E and ν are Young's modulus & Poisson's ratio of the cantilever material

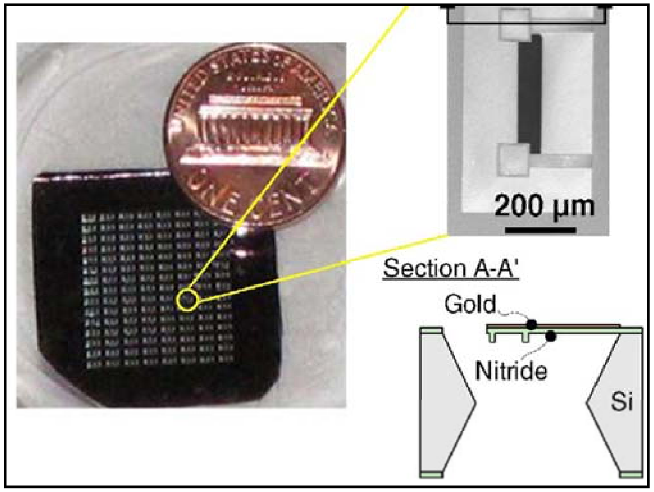
2-D cantilever array system with optical readout



Cantilever design having flexible beam and rigid paddle regions



Reflected light spot on CCD image plane



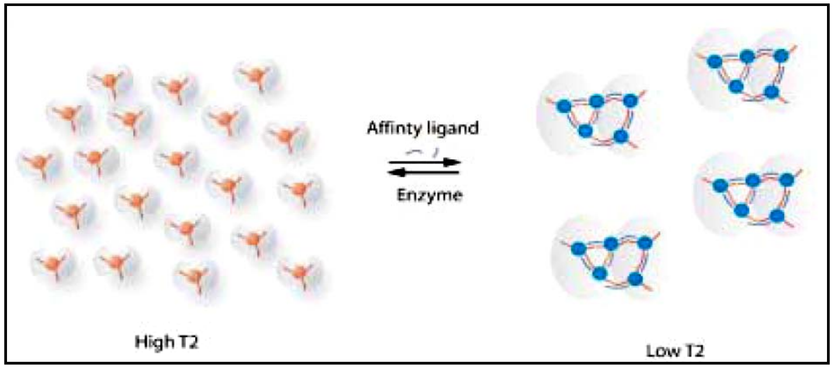
The chip has about 720 microcantilevers

Silicon nitride cantilever of 200 µm long, 0.5 µm thick, with E = 85 GPa, v = 0.27, a surface stress change of 1 mJ/m^2 will result in a deflection of 4 nm at the cantilever end, which can be easily detected using an optical readout system similar to that of atomic force microscope

Magnetic Nanoparticles as Nanosensors

➢ Upon target binding, these nanosensors cause changes in the spin - spin relaxation times of neighboring water molecules, which can be detected by magnetic resonance (NMR/MRI) techniques

➢ These magnetic nanosensors have been designed to detect specific mRNA, proteins, enzymatic activity, and pathogens (e.g., virus) with sensitivity in the low femtomo le range (0.5 ± 30 fmol)

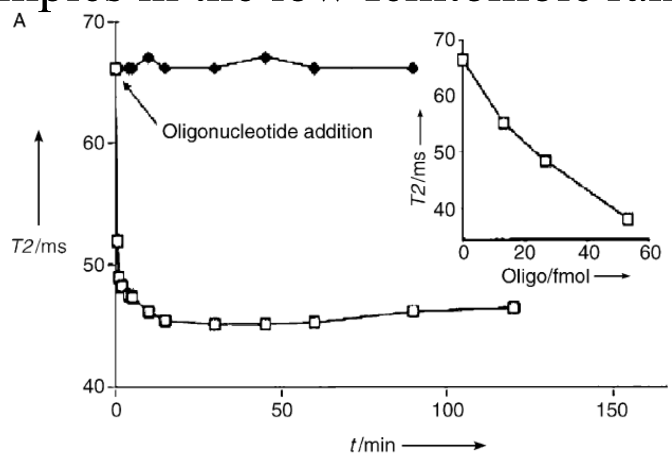


3 - 5 nm monocrystalline iron oxide nanoparticles (MION)

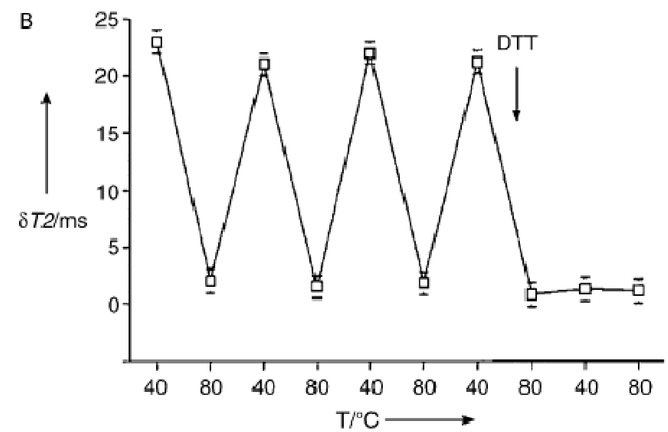
Diagram of the magnetic nanosensors acting as magnetic relaxation switches. Superparamagnetic nanoparticles self-assemble in the presence of a target with a corresponding decrease in the solution T2 relaxation time. Self-assembled nanoparticles can be dispersed by the action of an enzyme, temperature or pH change depending on the nature of the bond holding the nanoassembly together.

Magnetic nanosensors for detecting DNA

- Cluster formation of magnetic nanoparticles, upon addition of a complementary oligonucleotide, resulted in a quick and significant decrease in the spin- spin relaxation times (T2) of neighboring water molecules, at 40 ºC (Figure A)
- When a non complementary oligonucleotide was used, no change in T2 was observed
- At 1.5 T, significant differences were readily apparent by MRI between the samples in the low femtomole range (0.5 - 2.7 fmol)

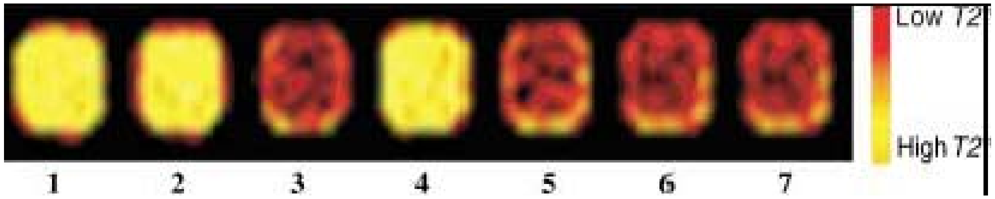


A. Temporal change of water T2 relaxation times with (□) and without (♦) complementary oligonucleotide. Insert shows the effect of increasing concentrations of oligonucleotides on water T2



B. T2 changes (T2) of an aqueous solution of nanosensors as a function of temperature cycling

Magnetic nanosensors for measuring various enzymatic activities including restriction endonucleases, methylases, and proteases



NMR imaging of enzymatic activity

- BamHI (from *Bacillus amyloli*) is a type II restriction endonuclease, having the capacity for recognizing short sequences (6 b.p.) of DNA and specifically cleaving them at a target site.
- Restriction endonuclease detection using a pair of nanosensors with complementary oligonucleotides (1 and 2)
- When mixed in solution the oligonuleotides hybridize causing the nanosensors to cluster (3).
- BamHI sensitive nanoassembly, with a corresponding decrease in T2, is formed upon treatment with BamHI, the nanoassemblies disassemble, and an increase in T2 is observed (4)
- Treatment with other restriction endonucleases (EcoRI, HindIII, DpnI) do not cause a change in T2 of the solution (5, 6, 7)

Optical Nanosensors

- Luminescence (specifically, fluorescence) is commonly used in optical chemical-sensing techniques

- The inherent sensitivity of fluorescence analysis is well known and, because of this, it is often used for trace analysis

- Owing to the small size of the sensors, the sampling volume was reduced by more than six orders of magnitude over conventional sensors, making it ideal for subcellular measurements

Example

Nanobiosensors for the detection of nitric oxide via the fluorescence detection of cytochrome c', or fluorescently labeled cytochrome c' (a variant of cytochrome c in which the heme group is bound by two cysteines)

Salient features:

- ✓ Fast response time (<1 s), reversible, and linear up to 1 mM nitric oxide

- ✓ Detection limit is 20 μM, making the sensor useful for some biological samples

Probes Encapsulated By Biologically Localized Embedding (PEBBLEs)

Optical sensors that contain dyes whose fluorescence is quenched in the presence of the analyte to be determined

✓ Senses ions (H^+, Ca^{2+}, K^+, Na^+, Mg^{2+}, Zn^{2+}, Cu^{2+}, Cl^-) in cellular environments due to their small size (20 to 600 nm in diameter) and protect the sensing elements (i.e. fluorescent dyes) by encapsulating them within an inert matrix

✓ The selectivity and sensitivity of these nanosensors are comparable to those of macroscopic ion selective optodes, and electrodes, while the response time and absolute detection limit are significantly better

X In most practical applications, these PEBBLE sensors have been problematic because of signal fluctuations that were not directly caused by the concentration of the analyte. These fluctuations can be due to light scattering or to fluctuations in the excitation source (i.e. the higher the excitation power, the greater the intensity of the fluorescence)

✓ Ratiometric PEBBLE sensors overcome this problem. In this kind of sensor, a fluorescent indicator dye and a fluorescent reference dye are encapsulated inside the inert matrix. The sensor response is based on intensity ratios between the indicator and reference dyes

Ratiometric PEBBLE sensors for ions: pH, calcium, zinc, and magnesium

The dynamic range and selectivity of the PEBBLE is dependent on the dissociation constant (K_D) of the dye (C) with respect to the analyte and any interfering ions

The response mechanism and a description of K_D for calcium sensors are

$$[Ca^{2+}]_{(aq)} + C_{(acrylamide)} \leftrightarrows [C(Ca)^{2+}]_{(acrylamide)}$$

$$K_D = \frac{[C]_{(acyrlamide)}[Ca^{2+}]_{(aq)}}{[C(Ca)^{2+}]_{(acylamide)}}$$

Calibration of three calcium selective dyes and the corresponding polyacrylamide PEBBLE sensor

pH indicator	Linear range (μM calcium)	Slope ± S.D.	Intercept	r^2	n
Calcium Green + SR (dye)	0–0.15	11.7 ± 1.6	1.7	0.94	4
Calcium Orange + SR (dye)	0–0.15	1.5 ± 0.03	1.0	0.95	6
Calcium Green 5N + SR (dye)	3–30	0.010 ± 0.05	0.99	0.95	7
Calcium Green + SR (PEBBLEs)	0–0.15	7.3 ± 0.05	0.97	0.99	6
Calcium Orange + SR (PEBBLEs)	0–0.1	1.3 ± 0.05	1.0	0.79	5
Calcium Green 5N + SR (PEBBLEs)	0–5	0.022 ± 0.007	1.0	0.99	4

The slopes and intercepts correspond to the normalized fluorescence intensity, which is the fluorescence intensity of the Ca^{2+} indicator divided by the fluorescence intensity of the internal standard

Metal oxide nano-crystals for sensing

- Metal oxides possess a broad range of electronic, chemical, and physical properties that are often highly sensitive to changes in their chemical environment.

- The sensing properties of semiconductor metal oxide (nano-belts, nano-wires or nano-ribbons) assures improved selectivity and stability due to there crystallinity

- Their peculiar characteristics and size effects make them interesting both for fundamental studies and for potential nano-device applications, leading to a third generation of metal oxide gas sensors

Working principle of metal oxide gas sensors

1. Conductimetric metal oxide gas sensors rely on changes of electrical conductivity due to the interaction with the surrounding atmosphere
2. When a metal oxide is semiconducting, the charge transfer process induced by surface reactions determines its resistance

Sensing mechanism in metal oxide gas sensors is related to ionosorption of species over their surfaces

Ionosorbed species when operating in ambient air are oxygen and water

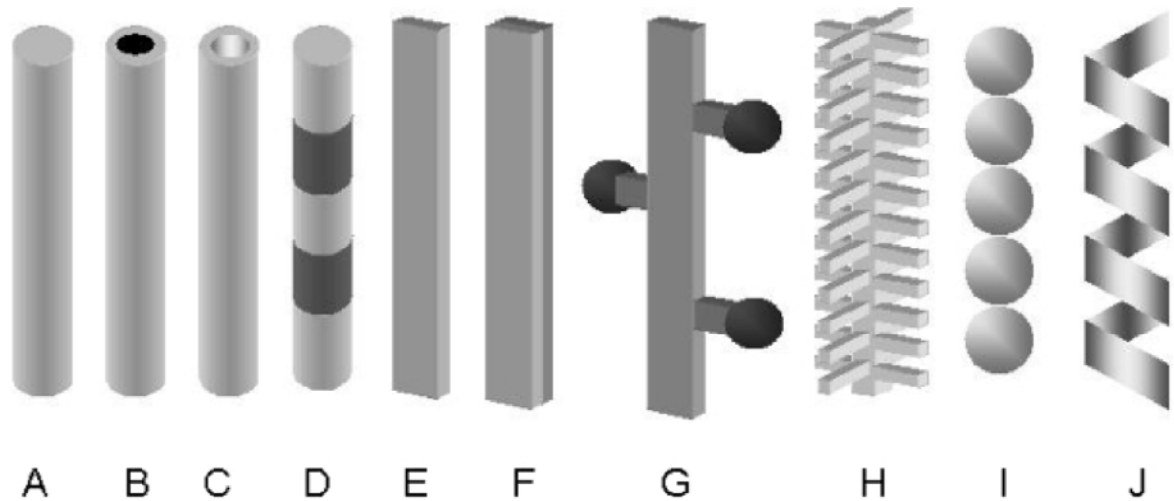
For some reducing gases, gas detection is related to the reactions between the species to be detected and ionosorbed surface oxygen

$$\mathrm{CO_{gas}} \rightarrow \mathrm{CO_{ads}}$$

$$\mathrm{CO_{ads}} + \mathrm{O_{ads}}^{-} \rightarrow \mathrm{CO_{2,gas}} + e^{-}$$

These consume ionosorbed oxygen and in turn change the electrical conductance of metal oxide

A schematic summary of the kinds of quasi-one-dimensional metaloxide nanostructures



(*A*) nanowires and nanorods; (*B*) core-shell structures with metallic inner core, semiconductor, or metal-oxide; (*C*) nanotubules/nanopipes and hollow nanorods; (*D*) heterostructures; (*E*) nanobelts/nanoribbons; (*F*) nanotapes, (*G*) dendrites, (*H*) hierarchical nanostructures; (*I*) nanosphere assembly; (*J*) nanosprings.

Oxide based Nano sensors

Metal oxide	**Target species**	**Salient features**	**Reference**
V_2O_5 nanofibres	1-Butylamine, toluene, propanol	Extremely high sensitivity was measured for 1-butylamine (below 30 ppb) and moderate sensitivity for ammonia. In contrast, only very little sensitivity was observed for toluene and 1-propanol vapours.	*Sens. Actuators B* 106 (2005) 730.
SnO_2 nanobelts	CO, NO_2, ethanol	Sensitivity at the level of a few ppb	*Appl. Phys. Lett.* 81 (2002) 1869.
In_2O_3 nanowires	NH_3, NO_2	The response times have been determined to be 5 s for 100-ppm NO_2 and 10 s for 1% NH_3, and the lowest detectable concentrations are 0.5 ppm for NO_2 and 0.02% for NH_3	*Appl. Phys. Lett.* 82 (2003) 1613.
ZnO nanowires	Ethanol	Sensitive to ethanol concentration is in the range of 1–100 ppm. Sensitivity increases sharply as the temperature is raised from 200 to 300 $^{\circ}$C	*App. Phys. Lett.* 84 (2004) 3654.
MoO_3 nanorods	Ethanol and CO	The detection limit for ethanol and CO is lower than 30 ppm	*Chem. Phys. Lett.* 407 (2005) 368
Cd-doped ZnO nanowire	Relative humidity	Cd-doped ZnO nanowires show a clear positive temperature coefficient of resistance effect, which is quite abnormal as compared to pure ZnO nanowires	*App. Phys. Lett.* **84** (2004) 3085.
SnO_2	Dimethyl methylphosphonate (DMMP)	Sensitive to 53 ppb DMMP and can be improved via doping nanobelts with catalytic additives.	*App. Phys. Lett.* 86 (2005) 063101.

Laser Nano Sensor measures thickness and roughness

Using auto focus principles with resolution as fine as 0.7 nm at speeds to 200 kHz, Laser Nano Sensor features spot size of 1–6 microns

It allows for displacement measurement within a few nanometers on quantifying surface roughness of any highly reflective surface

Available in 4 standard models, LNS sensor has measuring range of 0.00016–0.005 in. and operating distance from 0.09–1.0 in. Depending on target, accuracy ranges from 0.022–0.75 nm

Nano-sensors can warn of tsunamis

New technologies like nano-sensors with the ability to detect even a one-centimetre rise in waves could forewarn coastal areas of tsunamis, said M. Palaniswami, professor of Department of Electrical and Electronic Engineering, University of Melbourne.

Nanotechnological, inexpensive sensors that can detect invisible, odorless hydrogen leaks and sound the alarm wirelessly could help safeguard future vehicles and refueling stations based on the gas, experts told UPI's Nano World.

Miniaturized, thin film sun sensor for sun angle detection in space applications. The sun sensor has a field of view (FoV) of greater than 2π sr (±90º) and shall have a resolution of approximately 1º in elevation and azimuth angle. This sun sensor is therefore a coarse sun sensor with the advantage of having a large field of view. the photosensitive layer consisting of copper indium gallium diselenide (CIGS), the transparent conductive layer consisting of thin molybdenum or aluminum-doped zinc oxide, and its integrated design.

The Silicon AFM sensor with a tip radius of less than 10 nm contributed to many scientific breakthroughs

Nanosensor Probes Single Living Cells

The nano-needle of 50-nm-diameter silver-coated optical fiber that carries a helium-cadmium laser beam.

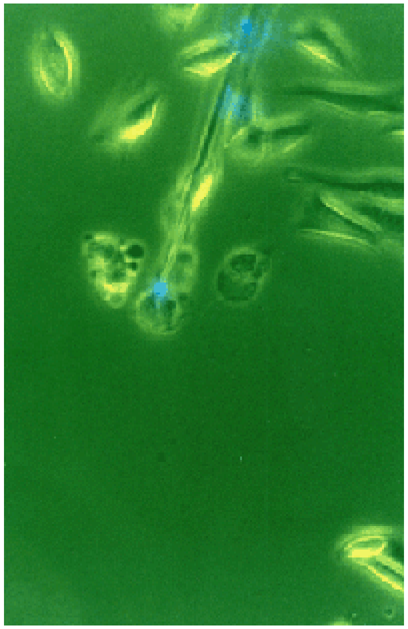
Attached to the optical fiber tip are monoclonal antibodies that recognize and bind to BPT.

The laser light, which has a wavelength of 325 nm, excites the antibody-BPT complex at the fiber tip, causing the complex to fluoresce.

The newly generated light travels up the fiber into an optical detector.

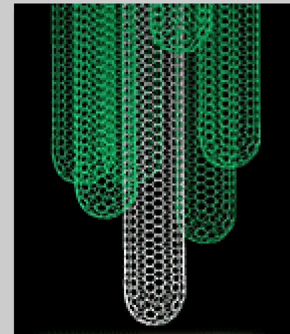
The layer of silver is deposited on the fiber wall to prevent the laser excitation light and the fluorescence emitted by the antibody-BPT complex from escaping through the fiber.

The ben-zo[*a*]pyrene (carcinogen) metabolite reacts with the cell's DNA, forming a DNA adduct, which can be hydrolyzed into a product called benzo(*a*)pyrene tetrol (BPT).



A nanosensor probe carrying a laser beam (blue) penetrates a living cell to detect the presence of a product indicating that the cell has been exposed to a cancer-causing substance

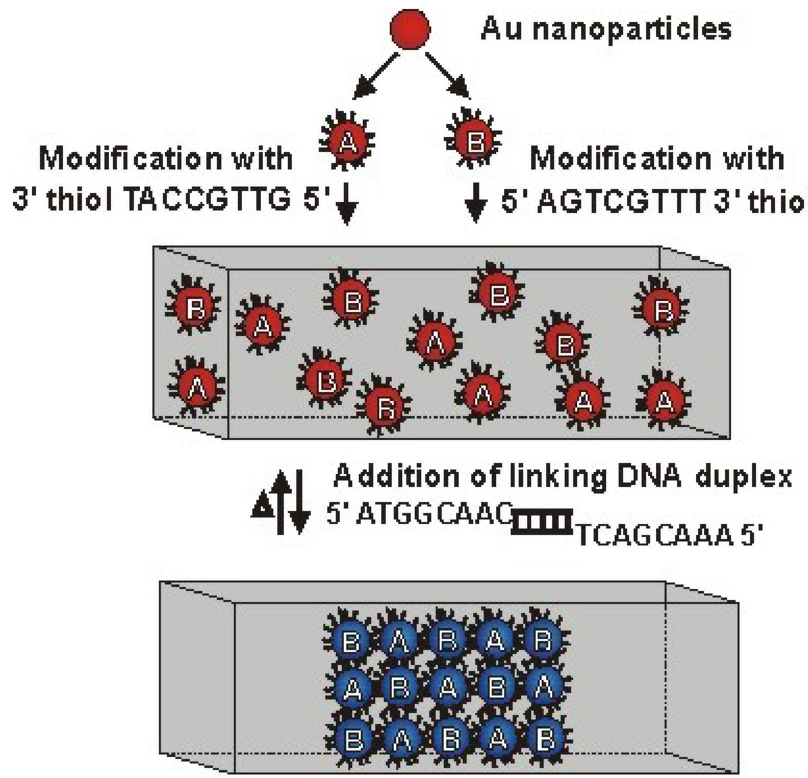
Sensors based on carbon nano-tubes can improve the detection of vapors from explosives. Sensors arranged in arrays will be tuned to respond to the presence of specific explosives and biological and chemical agents. Each nano-tube will be anchored to a metalized silicon substrate at one end of the tube and chemically functionalized to bind only to a specific molecule at the other end. The tube experiences a lowering of the frequency when an extra mass is attached to the functionalized end of the tube. The presence of a mass of an adsorbed agent, such as Anthrax, on the free end of the nano-tubes will produce a measurable frequency shift. The selective binding of agents to the chemically functionalized nano-tubes will allow the array to sense the presence of different BCX agents.


A Collection of Nanotubes
Source : CNI

Nanoparticles

DNA Nanoparticle Assembly

- NorthWestern University - Mirkin Group
- DNA-based nanoparticle assembly strategy
- By changing the DNA linker and the particle composition to design the physical characteristics of these materials.
- By hybridizing and dehybridizing the linking DNA to control the construction and deconstruction of the materials



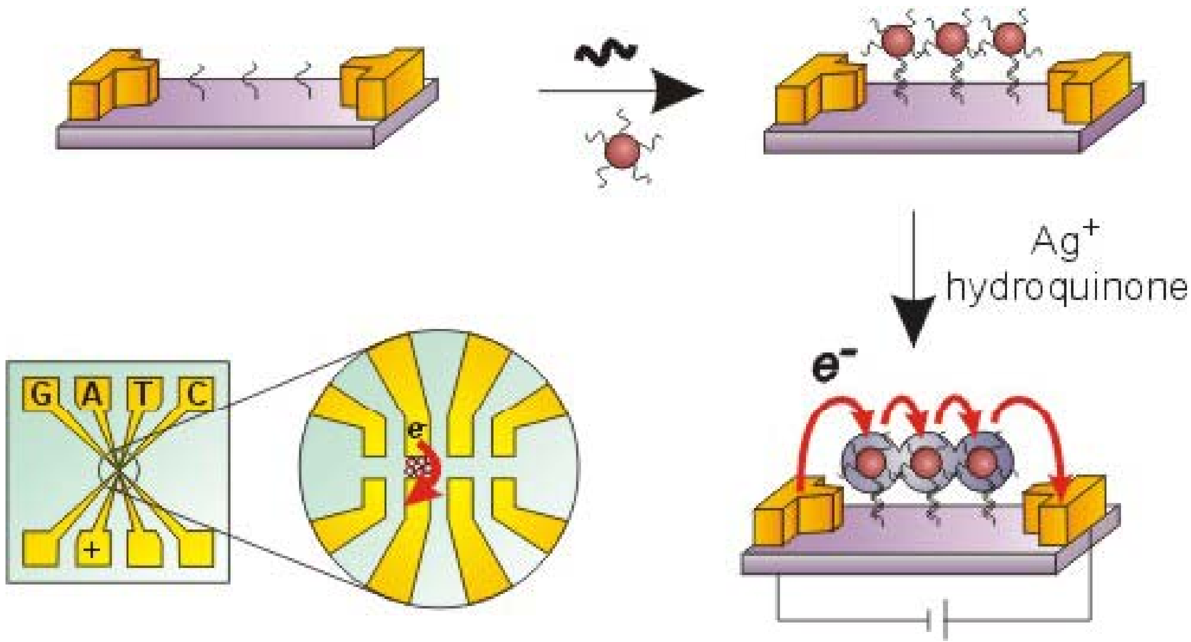
http://www.chem.nwu.edu/%7emkngrp/dnasubgr.html

http://pubs.acs.org/isubscribe/journals/jacsat/122/i19/pdf/ja993825l.pdf

Nanoparticles

"Gene Chips"

- Analyzing combinatorial DNA arrays.
- DNA detection scheme based on electrical properties of DNA-Au Nanoparticle assemblies.

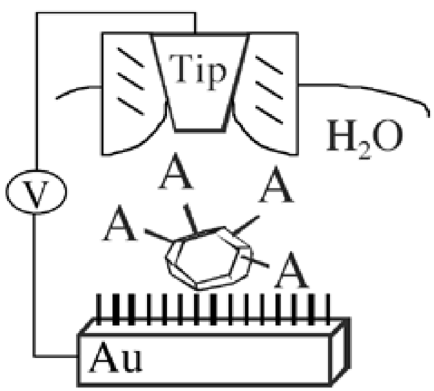


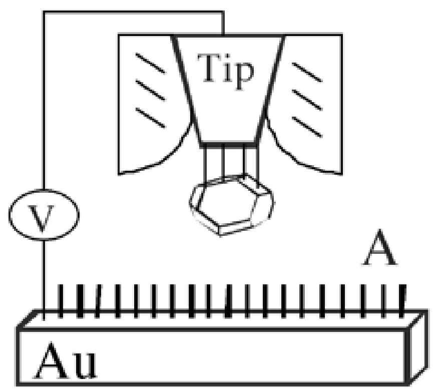
http://www.chem.nwu.edu/%7emkngrp/dnasubgr.html

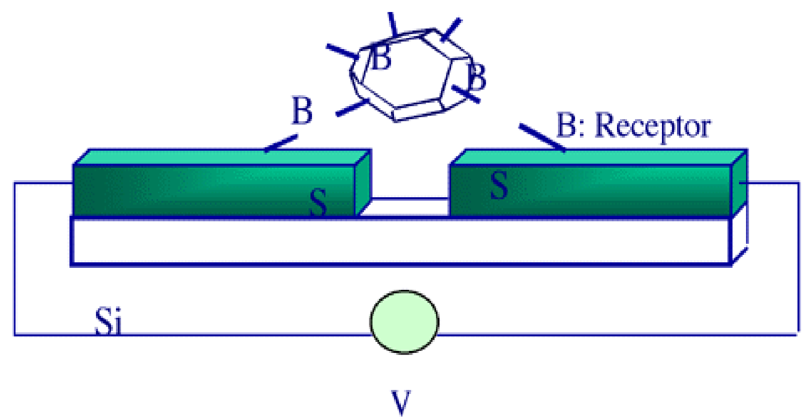
Nanoparticles

North Carolina State University - Feldheim Group

- 5 nm gold particles as chemical sensors
- Based on single electron tunneling
- Studying effects on surface chemistry





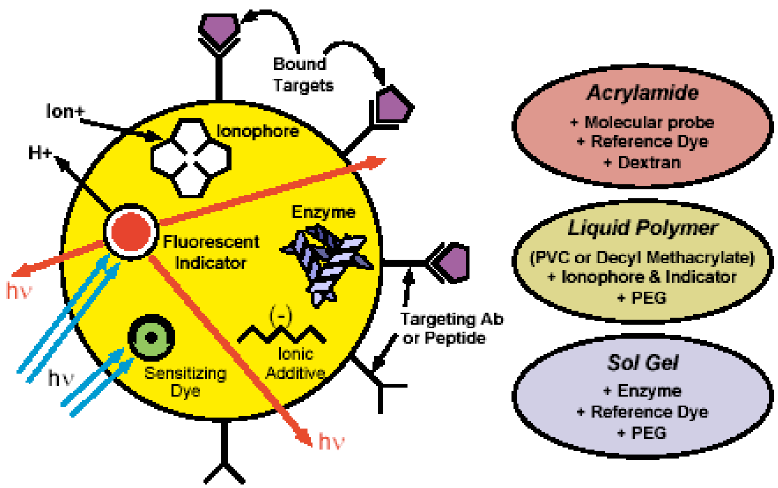


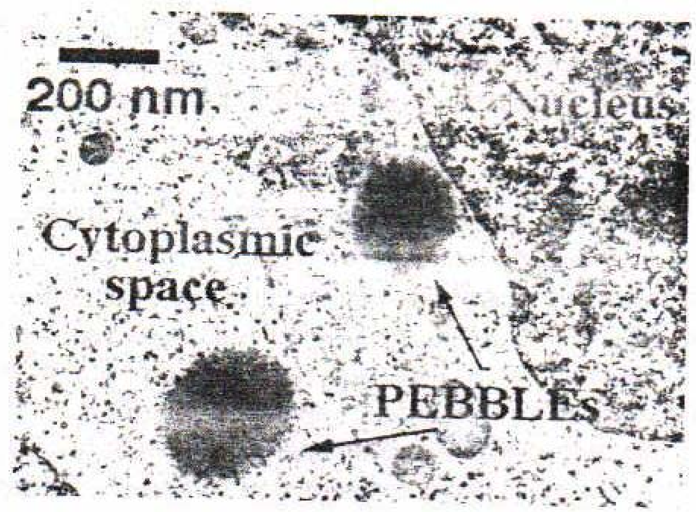
http://www.ncsu.edu/chemistry/dlf/nanoparticle.html

Nanoprobes

PEEBBLE probes (Probe Embedded By Biologically Localized Encapsulation)

- Sphere shaped 10nm+
- pH, calcium, magnesium, oxygen, potassium



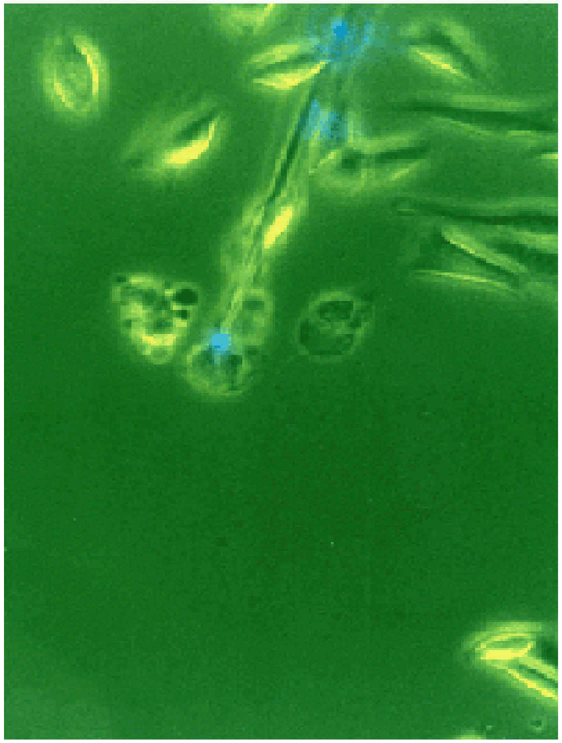


http://www.umich.edu/~koplab/research2/CRC_Review_try3pr.pdf

Nanoprobe

Nanosensor Probes Single Living Cells

- A 50-nm-diameter nanosensor probe carrying a laser beam (blue) penetrates a living cell to detect the presence of a product indicating that the cell has been exposed to a cancer-causing substance.
- This nanosensor of high selectivity and sensitivity was developed by a research group led by Tuan Vo-Dinh and his coworkers Guy Griffin and Brian Cullum.

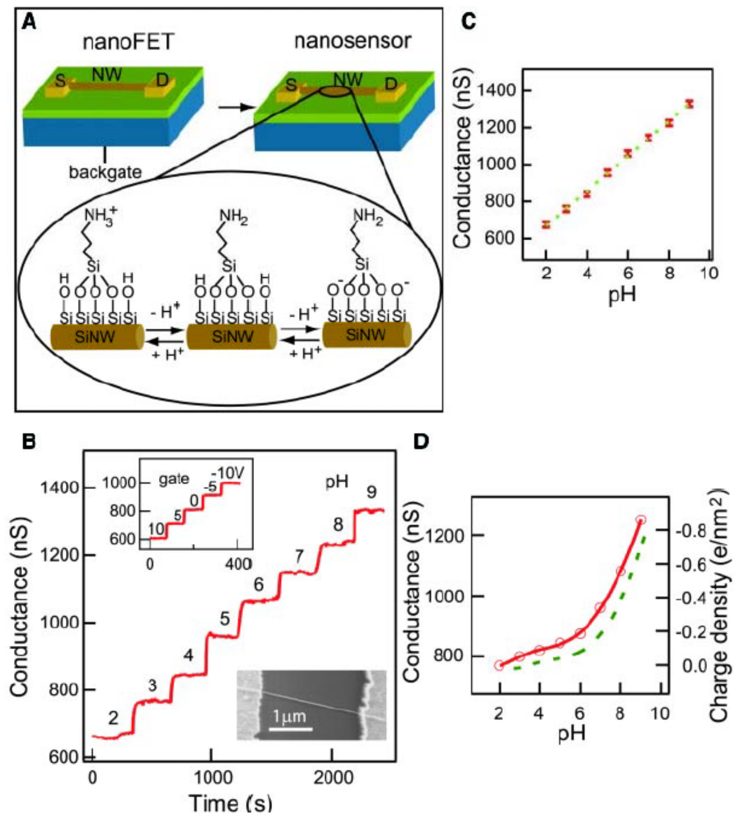


http://www.ornl.gov/ORNLReview/rev32_3/nanosens.htm

Nanowire Nanosensor

NW nanosensor for pH detection

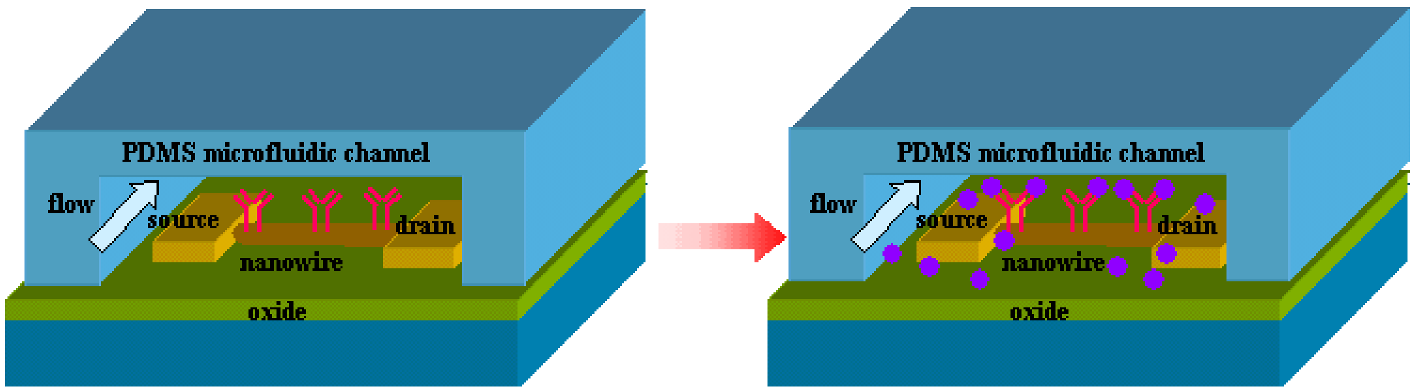
- A: Schematic illustrating the conversion of a NWFET into NW nanosensors for pH sensing. The NW is contacted with two electrodes, a source (S) and drain (D), for measuring conductance. Zoom of the APTES-modified SiNW surface illustrating changes in the surface charge state with pH.
- B: Real-time detection of the conductance for an APTES modified SiNW for pHs from 2 to 9
- C: Plot of the conductance versus Ph
- D: The conductance of unmodified SiNW (red) versus pH.



http://www.people.fas.harvard.edu/~hpark/Science_293_1289.pdf

Nanowire Nanosensor

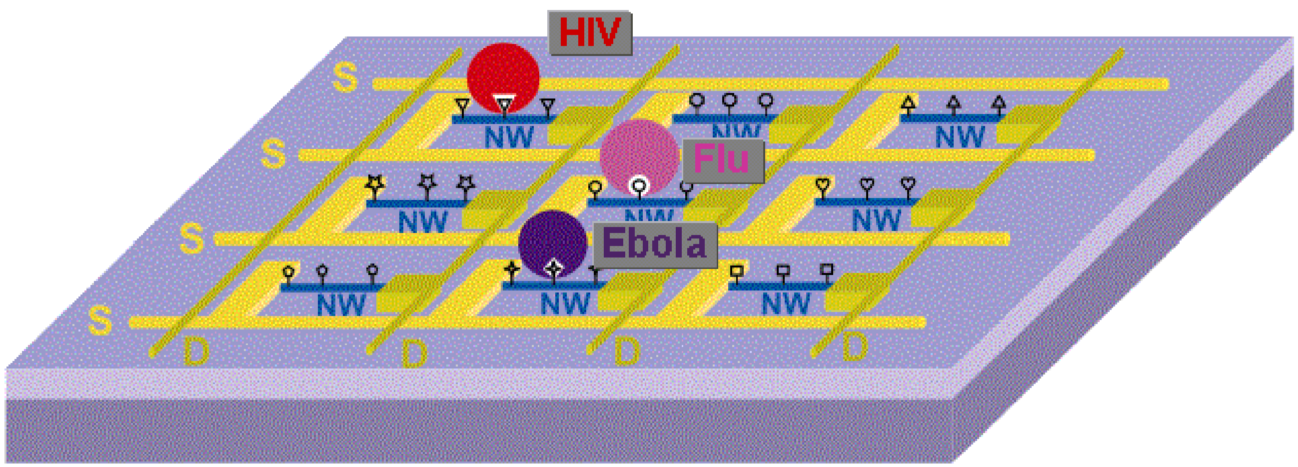
Nanowire Nanosensor: Real-Time Cancer Marker Detection



http://cyclotron.aps.org/weblectures/biology-physics/lieber/real/sld019.htm

Nanowire Nanosensor

Parallel Detection and Diagnosis of Viruses Using Integrated Nanowire Sensors



Nanowires modified with specific receptors can be assemble into integrated nano-biosensors for parallel detection and diagnosis of trace amount of dangerous viruses and other threats.

http://cyclotron.aps.org/weblectures/biology-physics/lieber/real/sld023.htm

From MEMS to NEMS

- MEMS are *micro*electromechanical systems
- NEMS: *nano*electromechanical systems or structures.
- Processes such as electron-beam lithography and nanomachining now enable semiconductor nanostructures to be fabricated below 10 nm. It would appear that the technology exists to build NEMS.

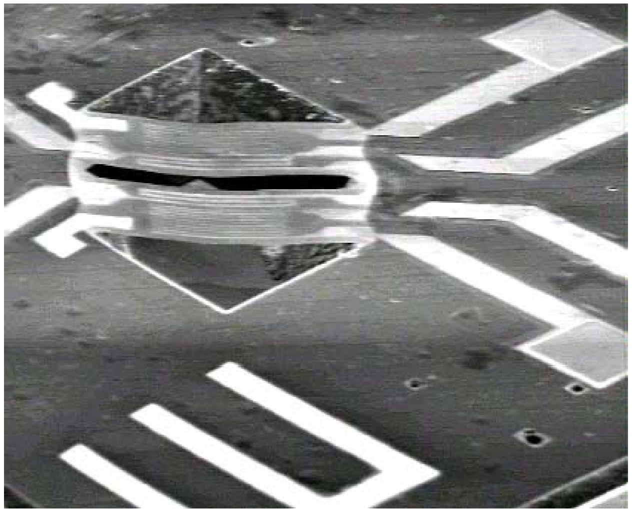
Challenges for NEMS

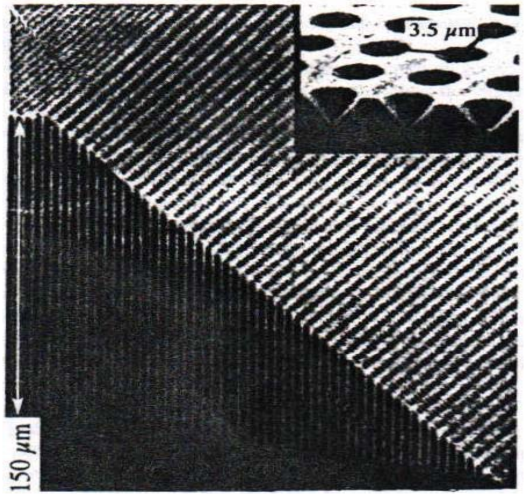
- Communicating signals from the nanoscale to the macroscopic world;
- Understanding and controlling mesoscopic mechanics;
- Developing methods for reproducible and routine nanofabrication.

http://physicsweb.org/article/world/14/2/8#pw1402082

Applications of Nanosensors

- Hot wire anemometer to measure fluid flow
- Thin film bolometers for IR radiation detection
- Capacitive humidity sensors - metal coated
- Photodetectors





Applications of Nanosensors

Ion-sensitive Field Effect Transistor (ISFET)

- A type of ion-sensitive sensor is derived from the MOSFET
- The working principle of this device is based on controlling the current that flows between two semiconductor electrodes. These "Drain" and "Source" electrodes are placed on one element, with the third electrode, the "Gate", between them.
- Measuring Ph in slaughtered meat is a good way to monitor product.

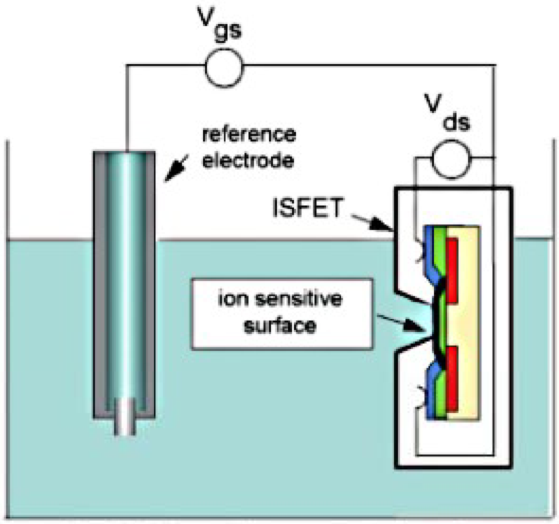
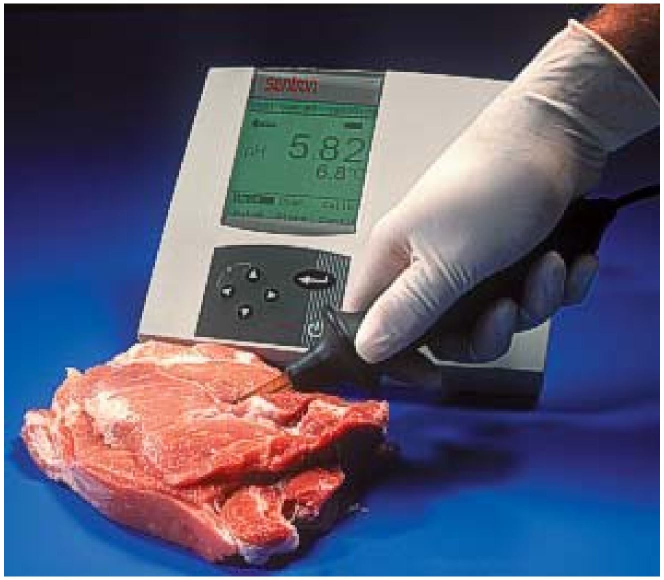


Fig.2: Schematic representation of an ISFET pH measuring system

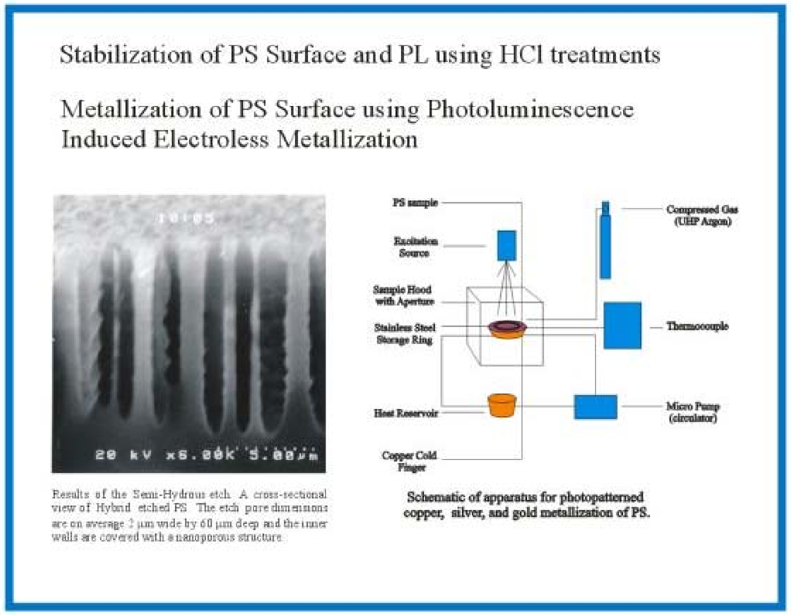


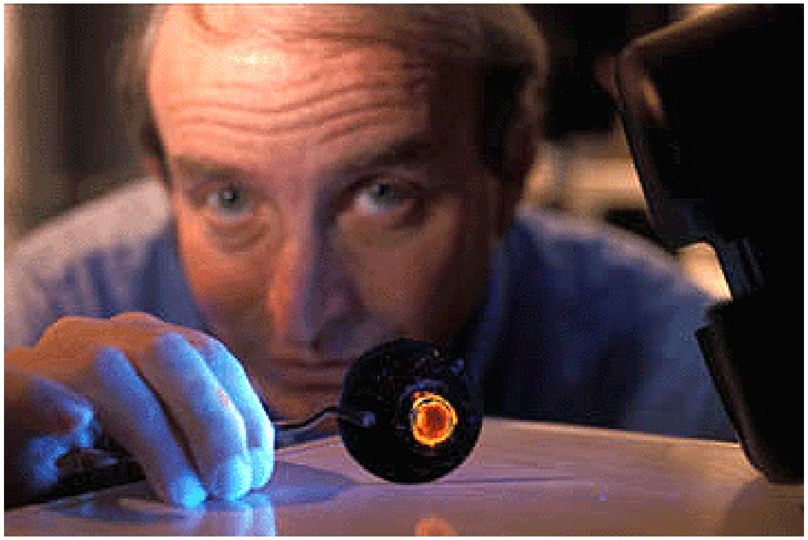
http://www.product-search.co.uk/internationallabmate.com/features/jan2002/sentron.shtml

Applications of Nanosensors

Porous silicon gas sensor.

- Novel Gas Sensors Based on Porous Silicon Offer Potential for Low-Voltage, Low-Cost Sensor Arrays Integrated with Electronics
- Developed by researchers at the **Georgia Institute of Technology**



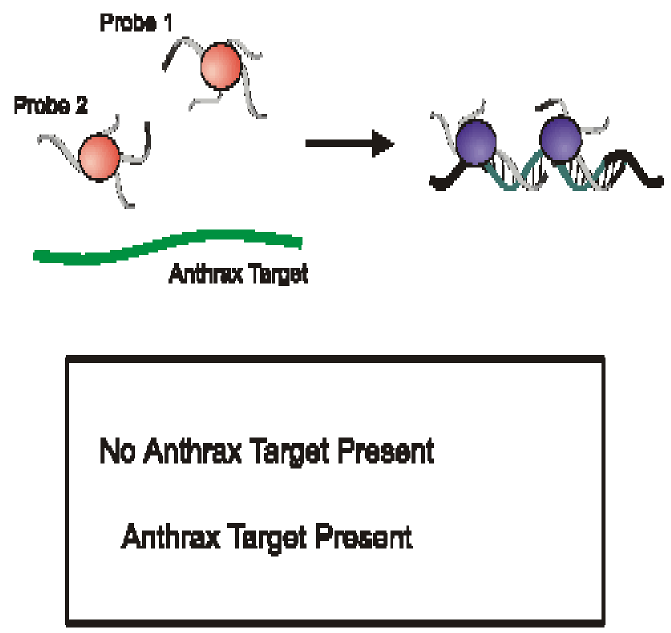


http://gtresearchnews.gatech.edu/newsrelease/SISENSOR.htm

Applications of Nanosensors

Biodetection

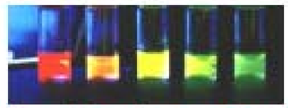
- A colorimetric sensor can selectively detect biological agent DNA;
- It is in commercial development with successful tests against anthrax and tuberculosis (Mirkin 1999).
- The sensor is simpler, less expensive and more selective—it can differentiate one nucleotide mismatch in a sequence of 24, where 17 constitutes a statistically unique identification.



http://www.wtec.org/loyola/nano/IWGN.Research.Directions/chapter08.pdf

Applications of Nanosensors

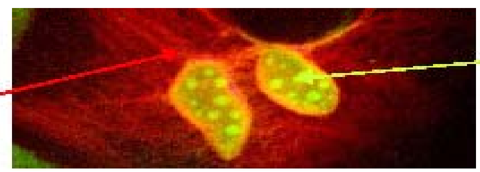
- Nanocrystals as Fluorescent Biological **Labels**



Band gap vs. size in CdSe nanocrystals
10 year study of scaling laws and synthesis

Unexpected applications in biological labeling
Example: Two-color stain of mouse fibroblast cell

5 nm crystals bound to actin fibers



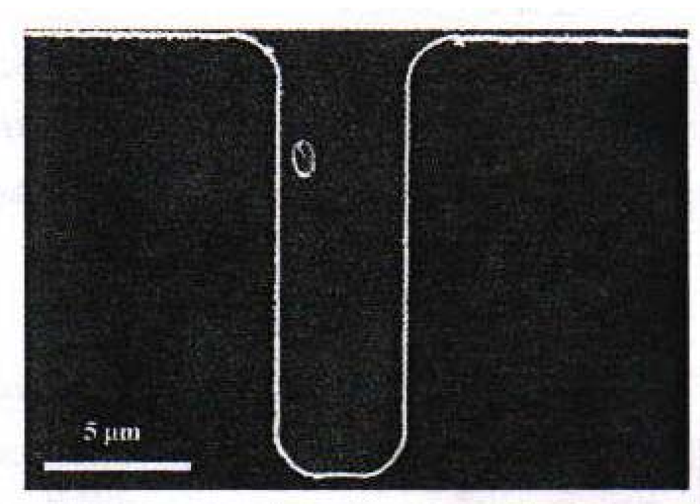
3.5 nm crystals bound to cell nucleus

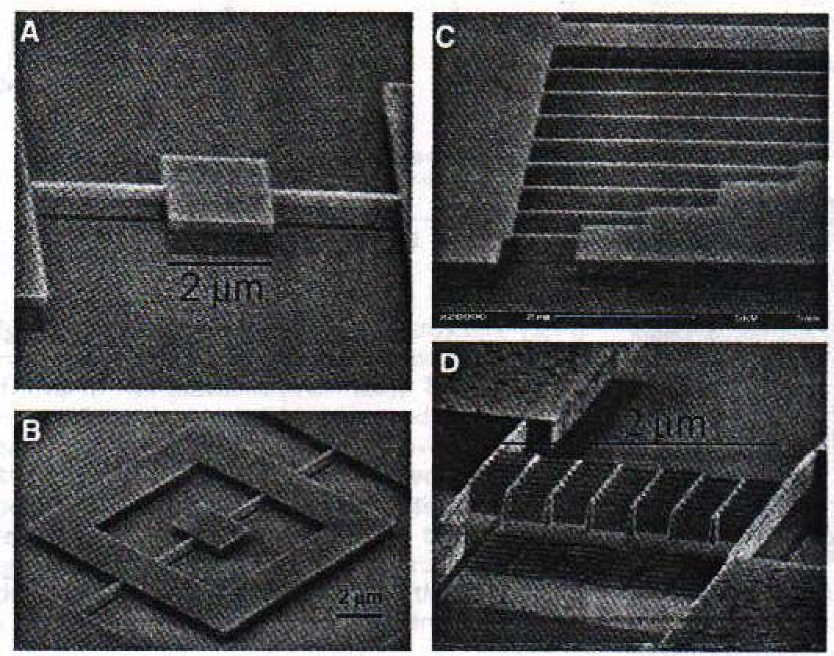
- Significant advantages over conventional dyes:
- Reduced photobleaching
- Multi-color labeling, parallel screening
- Infrared labels, blood diagnostics
- Molecular size nanocrystals are bio-compatible, with many other possible applications

Bruchez, M. Jr., M. Moronne, P. Gin, S. Weiss, and A.P. Alivisatos. 1998. Semiconductor nanocrystals as fluorescent biological labels. *Science* 281:2013-2016.

Future Nanosensors

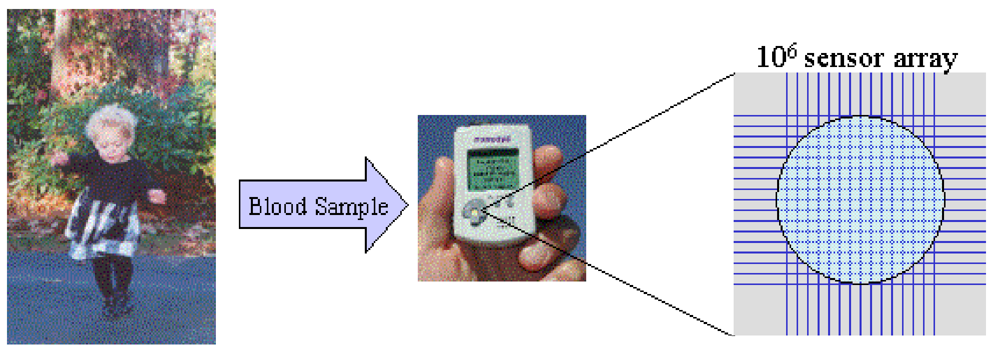
- Nanodevices - Nano Electro Mechanical Systems (NEMS)
  - NEMS oscillators (resonant sensors) used to detect
    - Magnetic forces of a single spin
    - Biomechanical forces
    - Adsorbed mass





Future Nanosensors

Enabling Personalized Medicine

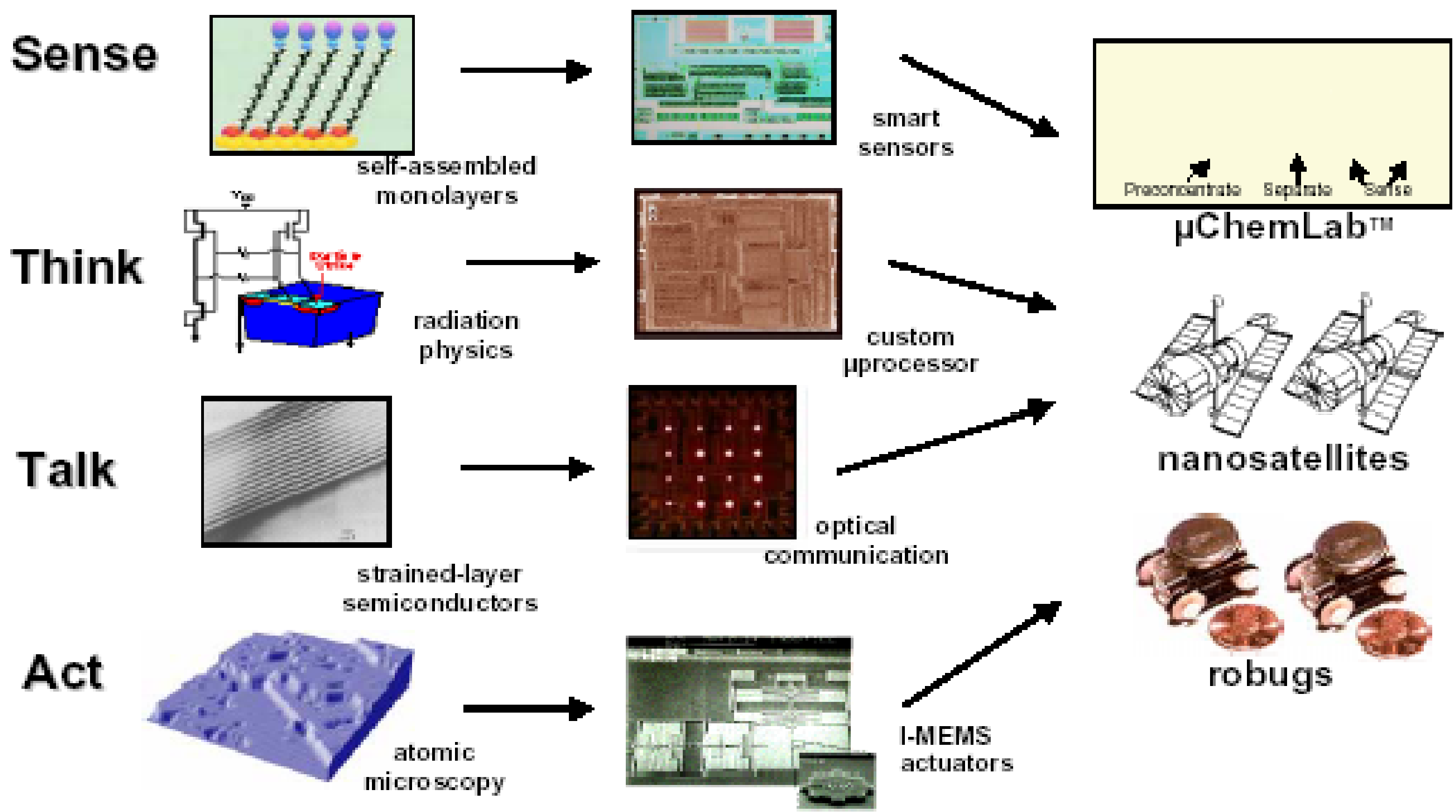


Detect simultaneously in real-time:

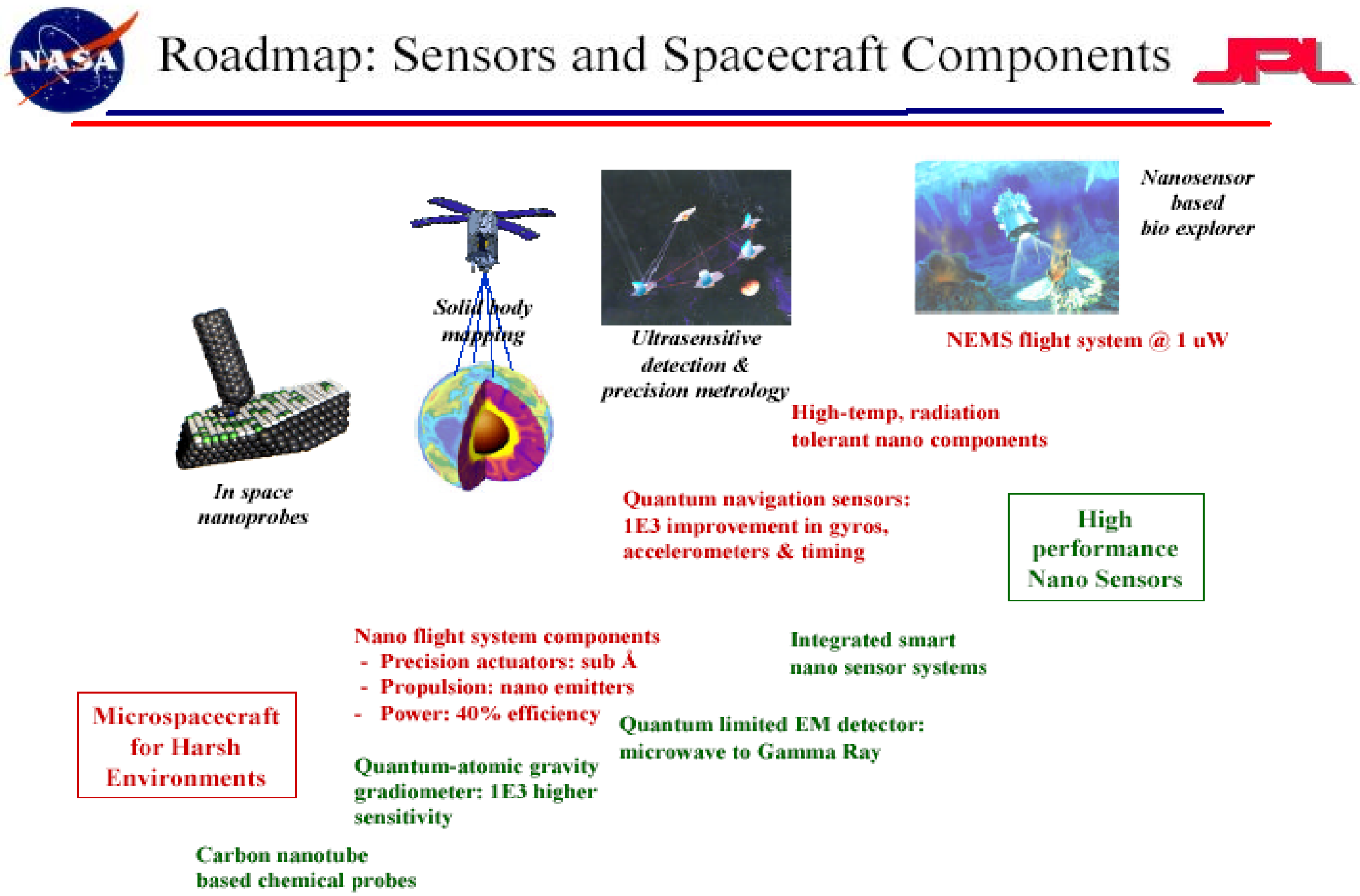
- all serum proteins & disease marker proteins
- viruses and pathogens
- screen genomic DNA for large or complete set of SNPs

http://cyclotron.aps.org/weblectures/biology-physics/lieber/real/sld025.htm

Future Nanosensors



Future Nanosensors



http://cism.jpl.nasa.gov/ehw/events/nasaeh01/papers/Toomarian.pdf

Conclusions

- Existing nanosensors have realistic applications
- Current envisioned nanosensors are still based on macrosensing techniques that are enhanced or miniaturized
- Future nanosensors will create paradigm shifts
- Enabling nanotechnology and future nanosensors will be possible with the development of nanoelectronics, and integratable nanodevices
- Nanosensors will ultimately have an enormous impact on our ability to enhance energy conversion, control pollution, produce food, and improve human health and longevity.

Questions

- What is Photoluminescence (PL)

  <u>Photoluminescence (PL) is simply the emission of photons from an excited molecular species.</u>

  Experiments show that the pores (openings) of PS can absorb and emit light when exposed to ultraviolet light. It was assumed that the PL property is induced by infrared multiphoton excitation. When oxidized, the photoluminescence is blue shifted with a peak intensity coming at approximately 625 nm.

- What is Electroluminescence (EL)

  <u>Electroluminescence (EL) is an optical phenomenon and electrotrical phenomenon where a material such as a natural blue diamond emits light when an electric current is passed through it.</u>

  Experiments show that electric current makes porous silicon glow red, so scientists look to it as a substitute for costly gallium arsenide in LEDs, since silicon is the second most common element in earth's crust. the fact that this material is translucent to visible light and is photoluminescent in the visible under UV light, due to quantum confinement effect.

Two good textbooks:

1. David K. Ferry and Stephen M. Goodnick, "Transport in Nanostructures," Cambridge University Press, 1997.

2. Mark Lundstrom, "Fundamentals of Carrier Transport," Cambridge University Press, 2000.

And a good review paper:

M. V. Fischetti et al., "Scaling MOSFETs to 10 nm: Coulomb effects, source starvation, and virtual source model," J. Computational Electronics, vol. 8, pp. 60-77, 2009.

Detectors for tomorrow

-Quest of knowledge and need of society-

detectors are being used from the beginning for detecting particles ranging from ~KeV to TeV.

Nuclear physics,
Solid State Physics,
High energy physics,
Health physics,
Medical diagonisis

Neutrons, photons,charged particles (light or heavy), muons, neutrinos…
Underground to nuclear physics labs,
India, Europe, USA..

Gas, solid state, scintillators are used for all these efforts,
Current vision proposals can be categorised as,

→ Solid state (silicon) as detecting medium and beyond
→ Gas as detecting medium.

Dream detector

Good position resolution

Good momentum resolution

Good timing resolution

High rate capability

Radiation hard

Rugged,

Easy to use,

Least noise.

R&D are continuing to improve any or all of these properties.
Any viison on detector development will be

→To improve by newer detetctor materials/ detection technique.

→Newer uses of the detectors for the society.

SILICON DETECTORS
Go from mm to micron

- **Tracking in very high density environment**
- **Vertex determination, need precision track position measurement**

Even though several materials are tried, Si is still mostly used.

Handling Si in highest granularity environment is a challenge.

Keeping in sync with world leaders,

We have developed Si-strip detectors for CMS experiment at CERN

(how many channels???)

Spin-off:

developed Si-PIN diode of various sizes.

Going ahead:

Double sided processing established.

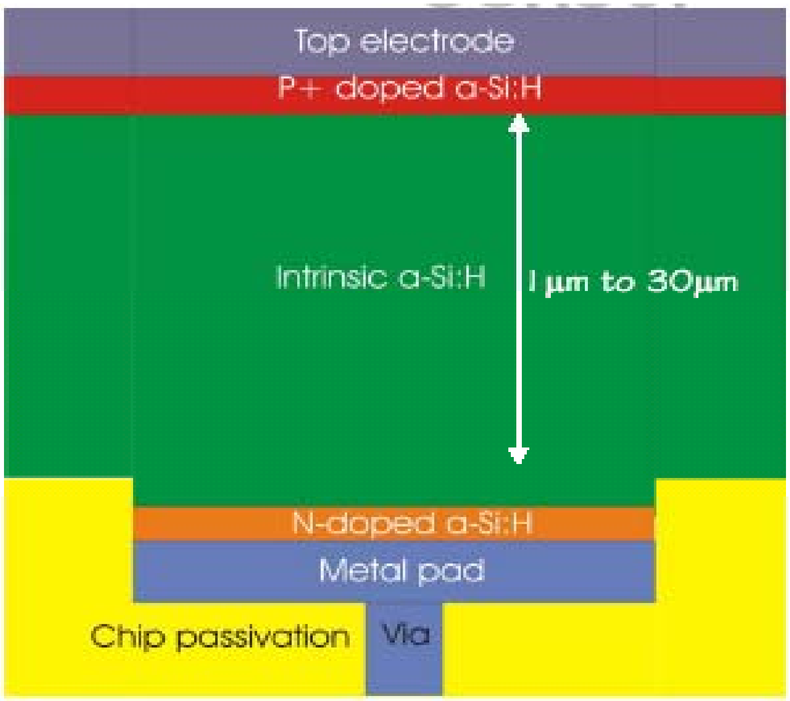
VISION FOR FUTURE

HEP scenario:
Participate in the core of HEP experiments for inner tracking.
→Cover LARGE AREA with double sided si-microstrip detectors
→ vertex determination with 50 micron resolution.
CBM experiment @ GSI new facility is the place of immediate interest.

Nuclear physics scenario:

- BARC Charged Particle Array for Nuclear Reaction Studies
- **108 detector modules to be configured as a spherical array**
- **Si-strip detectors to measure scattering angle and energy of charged particles**
- **CsI(Tl)-PIN diode detectors to measure residual energy of light charged particles which penetrate Si-strip detectors**

- **Amorphous silicon PIN diodes**
- **Deposition of amorphous silicon on ASIC readout might be a new technology for pixel sensors (low cost, radiation hardness, thin films)**
- **Silicon detector fabrication process becomes the backend processing of electronic wafer**
- **Technological issues to overcome - Deposition of high quality (low defects) thin film with thick intrinsic layer of 20mm**
- **Possibility of using amorphous silicon films along with scintillators for X-ray imaging**



One slide on Silicon detectors and society

Micro to NanoOne step ahead to Si-Pixel

Concept:

CNT junction diodes integrated with CNTFET-transistor (for first low-noise amplification) and CNT-conducting cables (for carrying charges to the read-out) can be grown on Si-wafer (substrate). The volume of read-out electronics can be further reduced with the help of nanoelectronics

Feasibility:

- Nano junction diodes and transistors are already in the scene. *p-n* junction diode has been developed at CNT-metal contact
- Nanotubular ropes composed of aligned multiwalled nanotubes having electrically insulating outer shells and semiconducting inner shells have been synthesized
- Vertically aligned CNTs have been deposited at predetermined position on pre-etched Silicon wafers

Realization:

- Nanotechnology is already a thrust area in the DAE-program
- Emphasis on R & D of CNT-based technology is expected
- Parallel initiative for indigenous development of the Pixel Detectors of present generation is sought for
- Finally, merging of the above three would make CNTISPD a reality

Gas detectors, vision from bright present to luminous future.

We have built:
Ionisation Chamber,
Proportional Counter,
GM Counter.

For URHIC,
High granularity gas proportional array,
→ 100,000 detecting cells each having $1cm^2$ area (STAR expt, BNL)
→ Large area position sensitive pad Chambers giving ~5mu position resolution. (ALICE expt, CERN)

Two proposals deal with gas detector development for materials research via SANS/SAXS/WAXS.

Other two takes the experience gained in HEP experience Forward.

Neutron detection:

- ***Small angle scattering signals are weak (need very low background)***
- ***requirement of low gamma sensitivity***

Towards an efficient and FAST SANS setup:

Physics goals of SANS:

→ Study size and shape of sample,

→ size distribution inhomogeneities

Conventional detectors need scanning over a region of interest, so time consuming.

Parallex problem makes the position determination for scatterd particles dificult.

For faster/efficient use of setup, proposed facility should have

→LARGE AREA POSITION SENSITIVE DETECTORS.

→Curvilinear array of modules to solve parallex problem.

- Large position sensitive detector of sensitive area 1 m^2
- He-3 gas based, pixel size 1 mm^2 to 1 cm^2, detection efficiency 70% to 100%
- Rate capability 10^8 Hz over Detector, time resolution better 1 µs

Multimodule curvilinear array of anode wires

- *2m arc length at 2m radius covers scan angle 60°*
- *wire spacing 1mm with automated wire mounting facility for higher accuracy*
- *Delay line method for pulse encoding and*
- *Individual wire screening for advantage of higher count rate capability.*

Microstrip detector as a module for curvilinear PSD

1) Higher accuracy of anode cathode dimensions and pitch because of lithography technique.

2) Higher gas gain and count rate

3) Good repeatability of modules and cost effective

Anode: 12mm , cathode: 300 mm

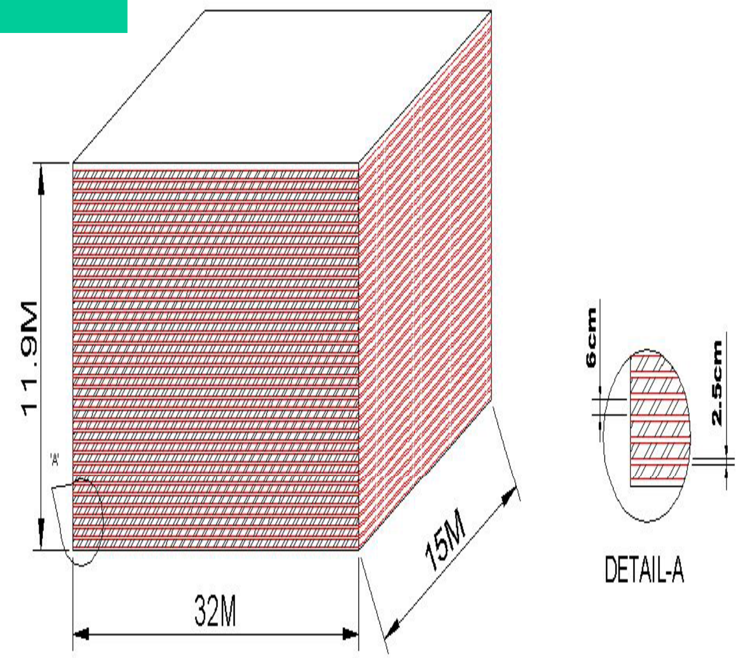
Anode Cathode spacing:150mm

Pitch: 612mm ,Sensitive area: 15 X 20mm

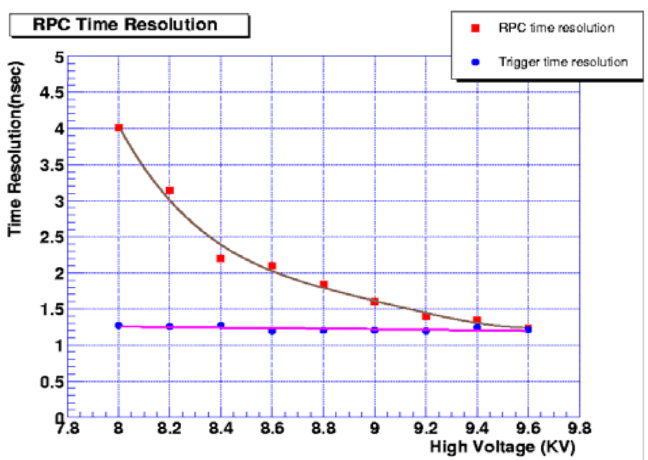
Towards higher energy –neutrino- Project of next decades –INO-

Need: Large area, high granularity, FAST,
Solution: RPC (WHY RPC?)

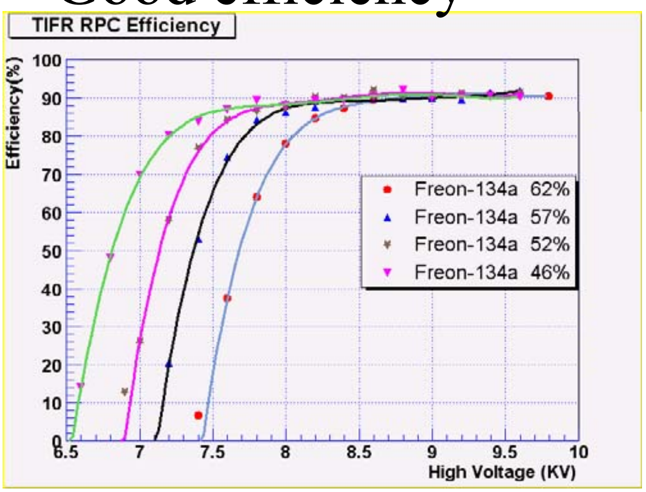
- Rugged, cheap and easy to produce large area cells,
- Good timing and spatial resolutions, rate capability and large signals
- Choice of designs, modes of operation and gases,
- Can do tracking, timing, particle identification and calorimetry
- Chosen for HEP experiments



Good timing

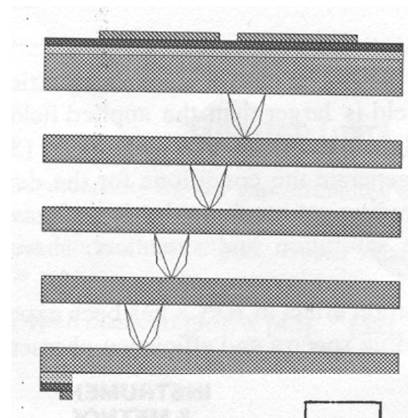


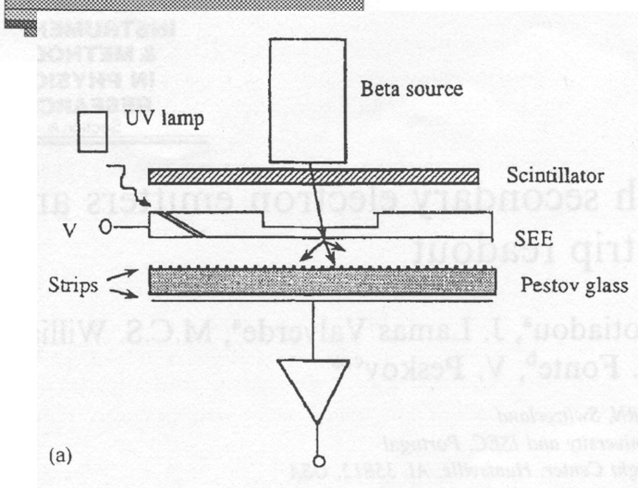
Good efficiency



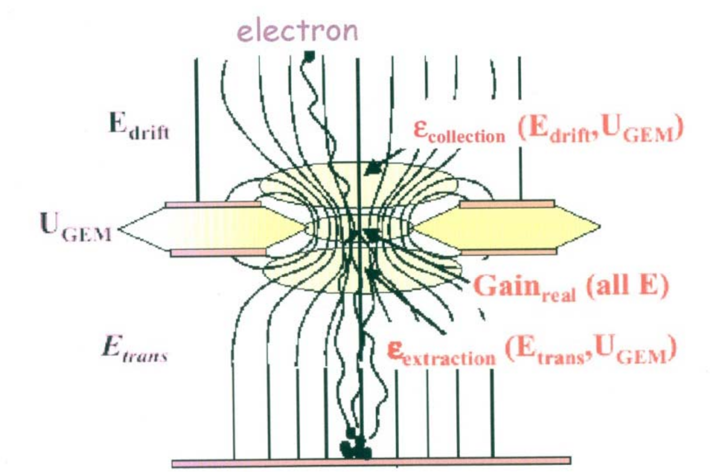
Proposal for new work

- Double-gap, multi-gap and hybrid designs
- Avalanche versus streamer modes of operation
- Gas mixture studies and optimization
- MIP signal and efficiency issues
- Improvement in time resolution
- Special RPCs for finer spatial resolution
- The all important ageing concerns





PRINCIPLE OF GAS ELECTRON MULTIPLIER (GEM)

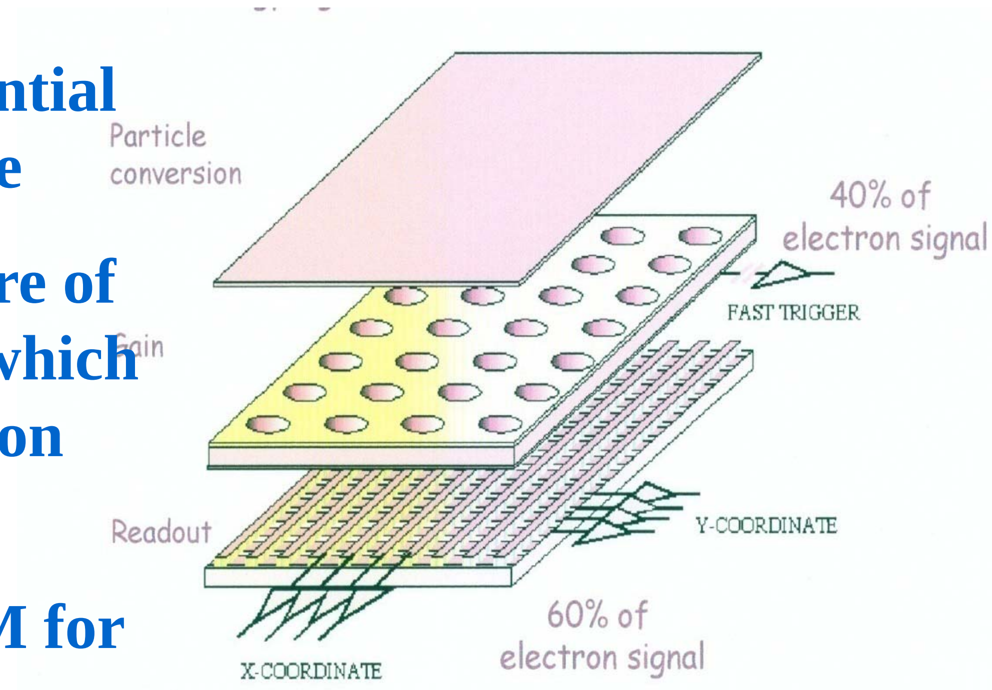


GEM foil consists essentially of a Polyimide foil (~50 um), copper clad (~5 um) on both side and perforated holes with typically 90-200um pitch and ~60 um diameter.

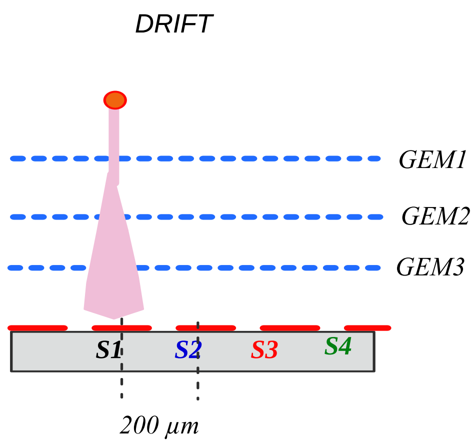
With the application of a potential typically 500 V between the

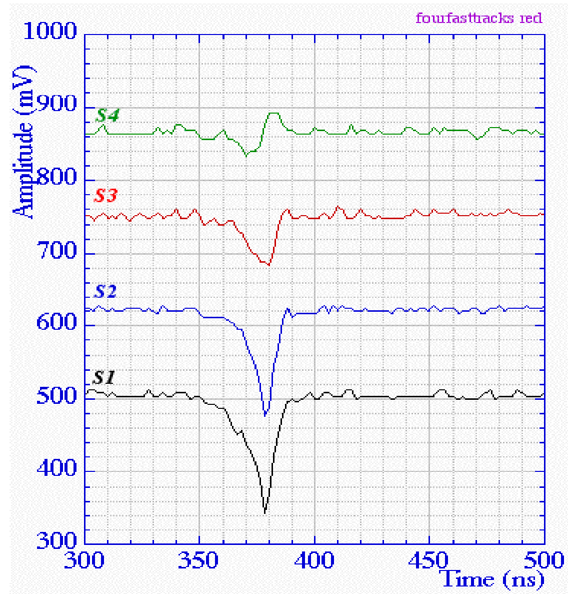
Two surfaces, the field at centre of each hole exceeds ~50KV/cm, which is sufficiently high for electron multiplication

Improved version- Triple GEM for high gain ~10^6



Improved multi-track resolution





Timing resolution: 12 nsec

Spatial resolution: 57 micron.

Proposed facility:

• Simulation on GEM and GEM based detector system

•Design and micro-pattern Generation, photo plotting of masks

•Fine Pitch Copper and polyimide etching and Gold plating

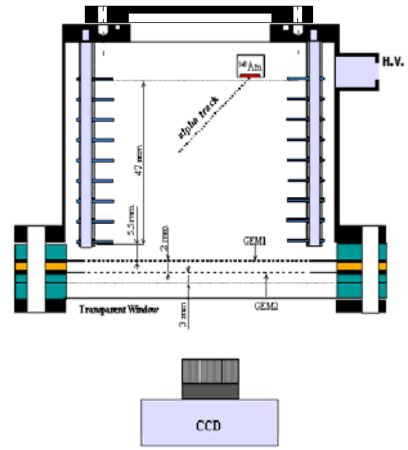
•Testing and assembly of of GEM foils (needs clean environment)

•R&D Lab and Industry interaction

•Use of Indigenous MANAS chip for GEM readout

Applications of detectors

- *QUEST of Knowledge: NP, SSP, HEP experiments, Astrophysics, Plasma monitoring, Beam monitor in accelerator.*



- *Optical imager*

- *GEM as PMT*