New Mountains to Climb:

New Phenomena, Materials and Technologies for the 21st Century

What are the new mountains?

Stone Age

Bronze Age

Iron Age

Age of Plastics

(21st Century)

Information Technology

What happens after silicon?

- Electronics
- Photonics
- “Plastic electronics”
- Organic polymer nanodevices*
- ?

* At least one dimension of which is ≤ 100 nm.
Wavelength of visible light: ~ 400 nm to ~ 700 nm.

Cheap "Throw-Away" Plastic, Paper Electronic Circuits

"Beginning of a New Era in Electronics"

<u>See</u>:

Philips Research Laboratories (The Netherlands); G.H. Gelnik, T.C.T. Genus and D.M. de Leeuw, App. Phys. Lett., 77(10), 1489 (2000) and references therein.

Lucent Technologies, (USA); A. Dodabalapur, Z. Bao, A. Makhija, J.G. Laquindanum, V.R. Raju, Y. Feng, H.E. Katz and J. Rogers, App. Phys. Lett., 73(2), (1998) and references therein.

D. Hohnholtz and A.G. MacDiarmid, Synth. Met., 121, 1327 (2001).

Organic/Polymer Integrated Circuits

Dodabalapur *et al., Appl. Phys. Lett*. 73, (1998) 142, (and refs. therein).
(Lucent Technologies, USA)

Microcontact Printing (Reel-to-reel)

- Circuits OK after 10,000 hours.
- All-organic 864 (FET) transistor circuit operating well after 5×10^8 cycles.

Line Patterning of Conducting Polymers*

New Approach for Inexpensive, Disposable Electronic Devices?

*Hohnholtz and MacDiarmid, Synth. Met., 2001, 212, 1327

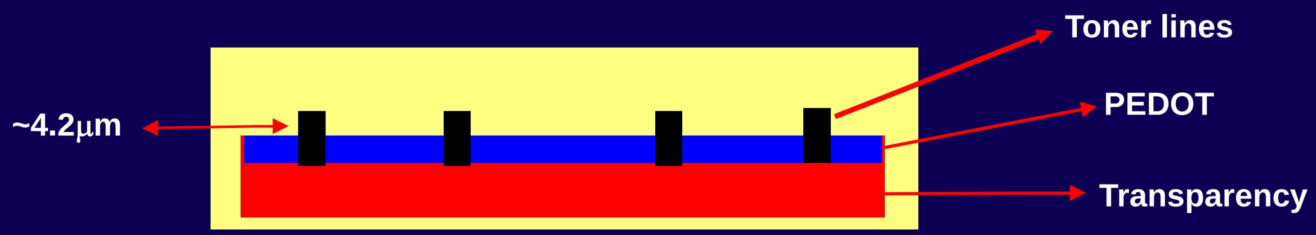
Line Patterning Does Not Involve Printing of (conducting) Polymers

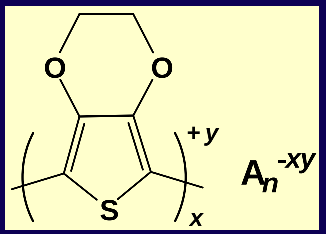
It is based on a completely new and different concept

A Different Approach

Exploit the observation that a commercial dispersion of polythiophene derivative (PEDOT) wets plastic transparency, but not the lines printed on the transparency by the office laser printer.*

- *Draw the pattern on the computer*
- *Print the pattern on the commercial transparency*
- *Apply by roller (1,2,3, …… as desired) coatings of PEDOT*
- *Dry (hot air gun) for 2-3 minutes between each coating*





"PEDOT"
A= Polystyrene sulfonate

**Bayer Co.*

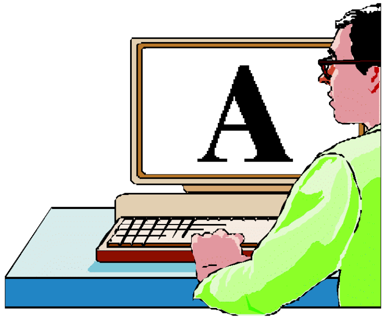
Line Patterning of Conducting Polymers*, Carbon Nanotubes$^{\gamma}$, and Metals on Plastics

New Approach for Inexpensive,

Disposable Electronic Devices?

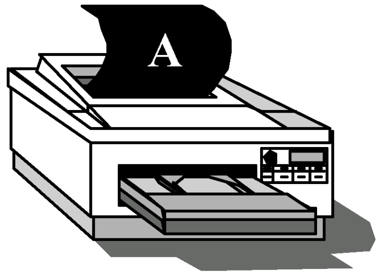
**Hohnholtz and MacDiarmid, Synth. Met., 2001, 212, 1327*
$^{\gamma}$Manohar et al., J. Amer. Chem. Soc., 2004, 126(14),4462

What is "Line Patterning" ?

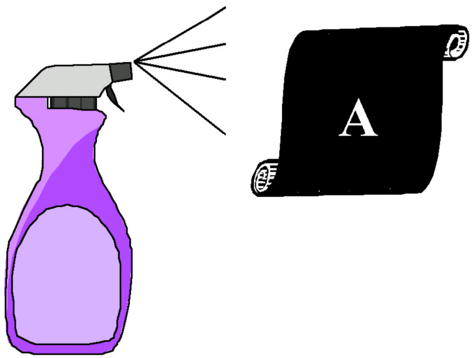


(1) Design

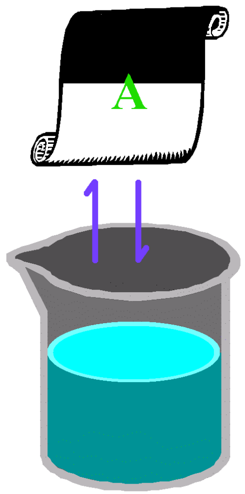
Inversion



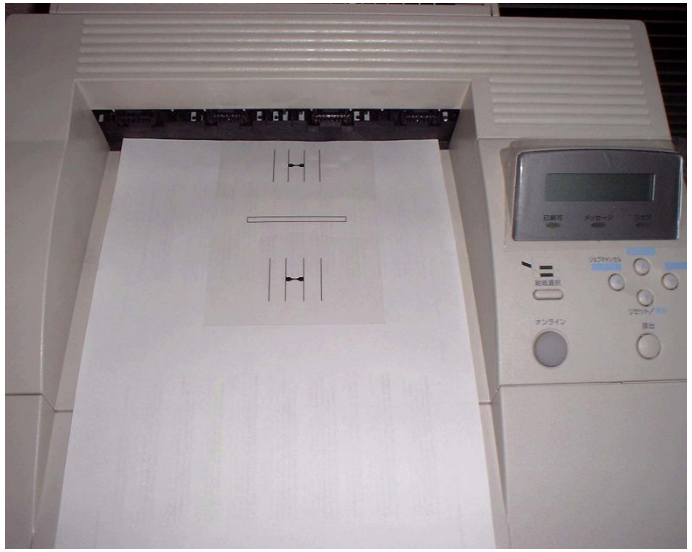
Printing

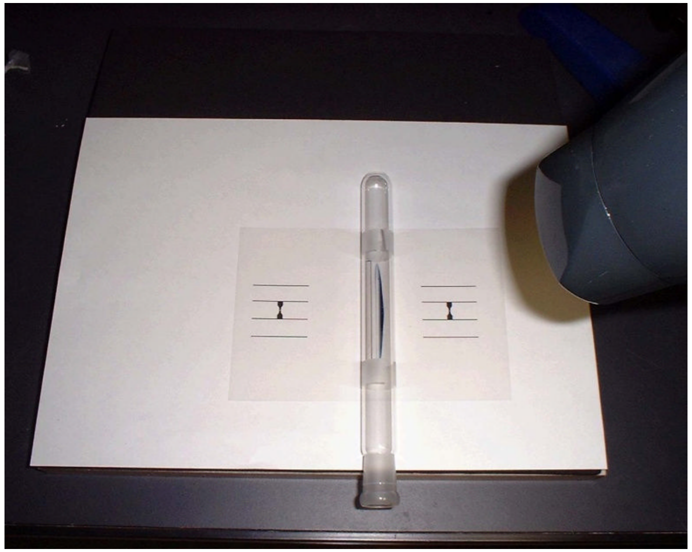


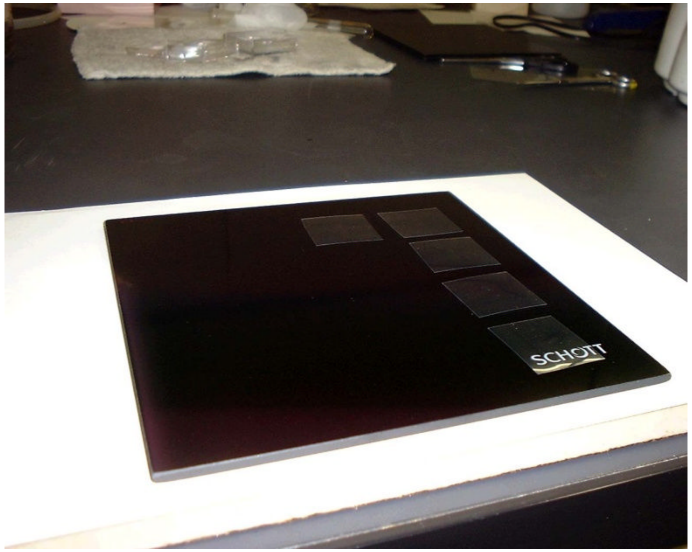
(2) Coating with
conducting polymer

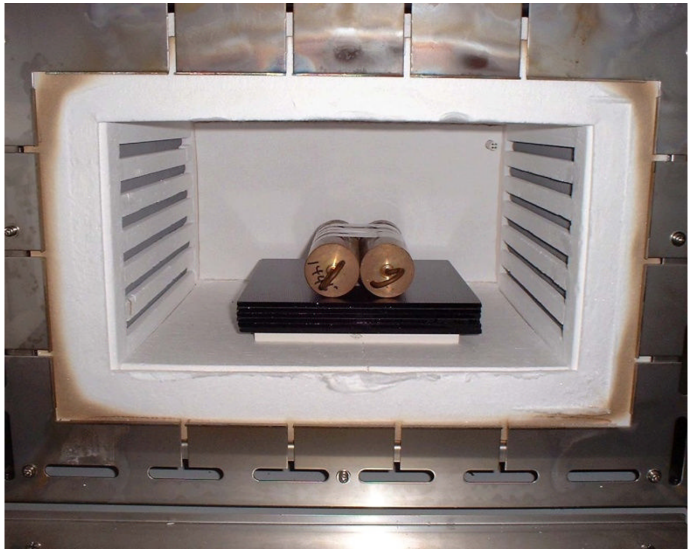


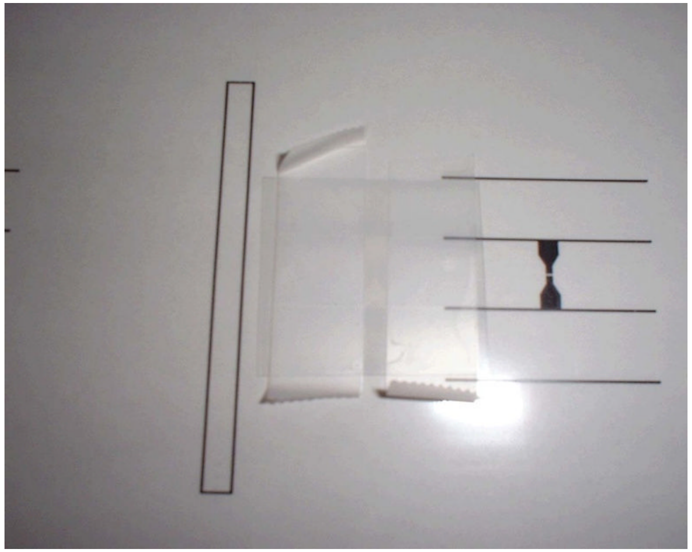
(3) Removal of printing

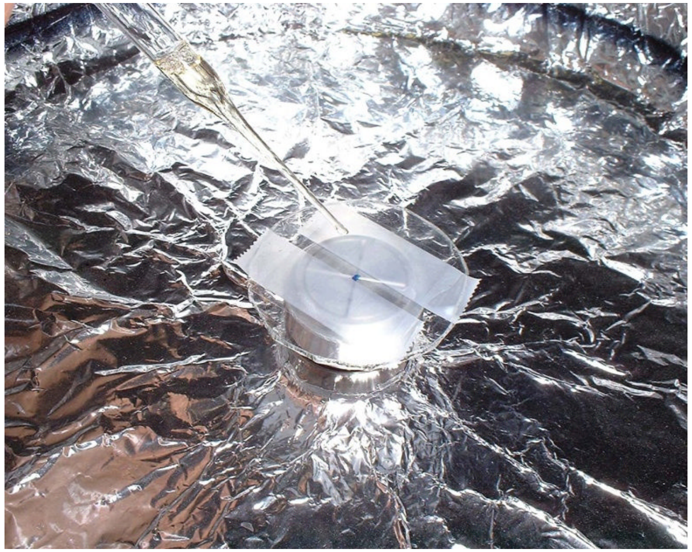




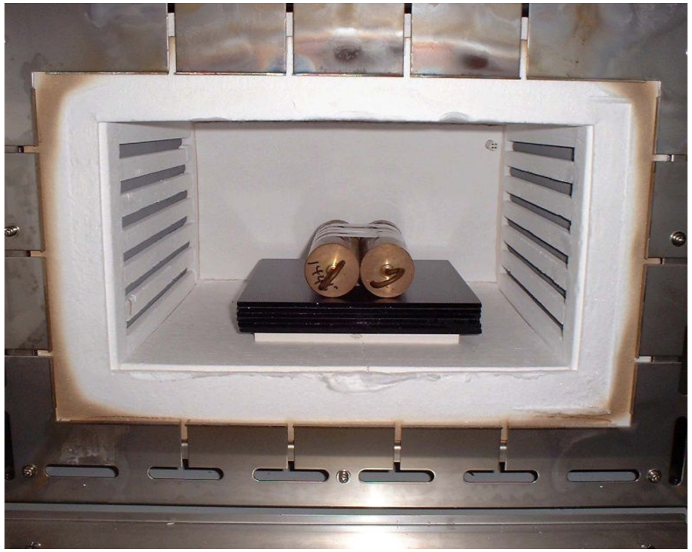

SCHOTT

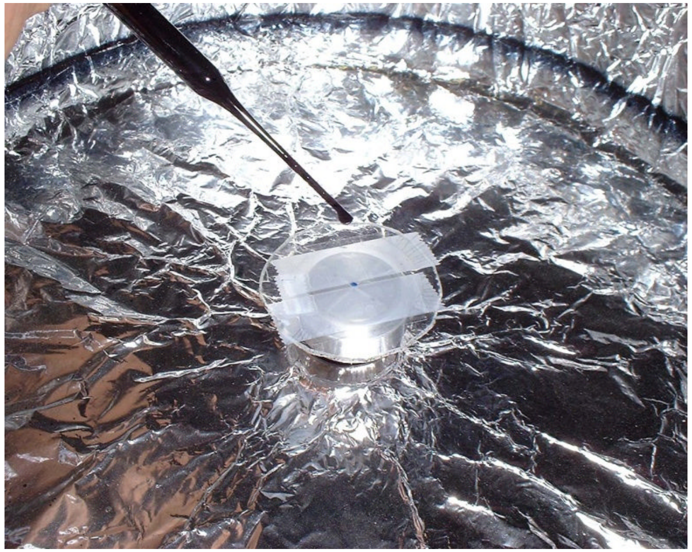


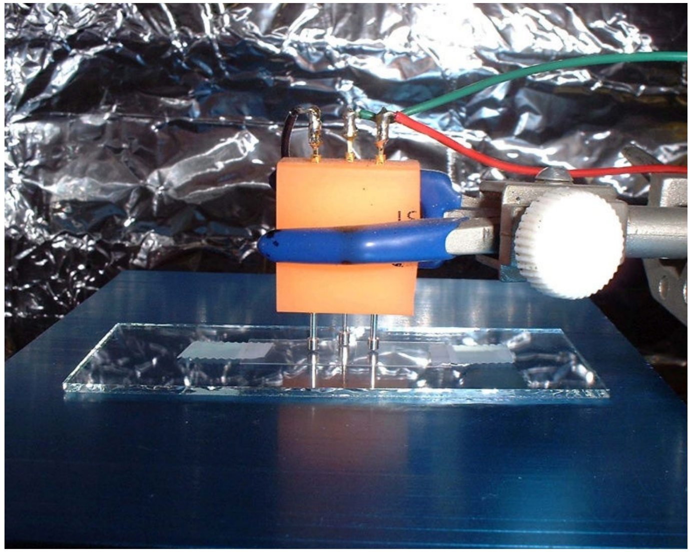




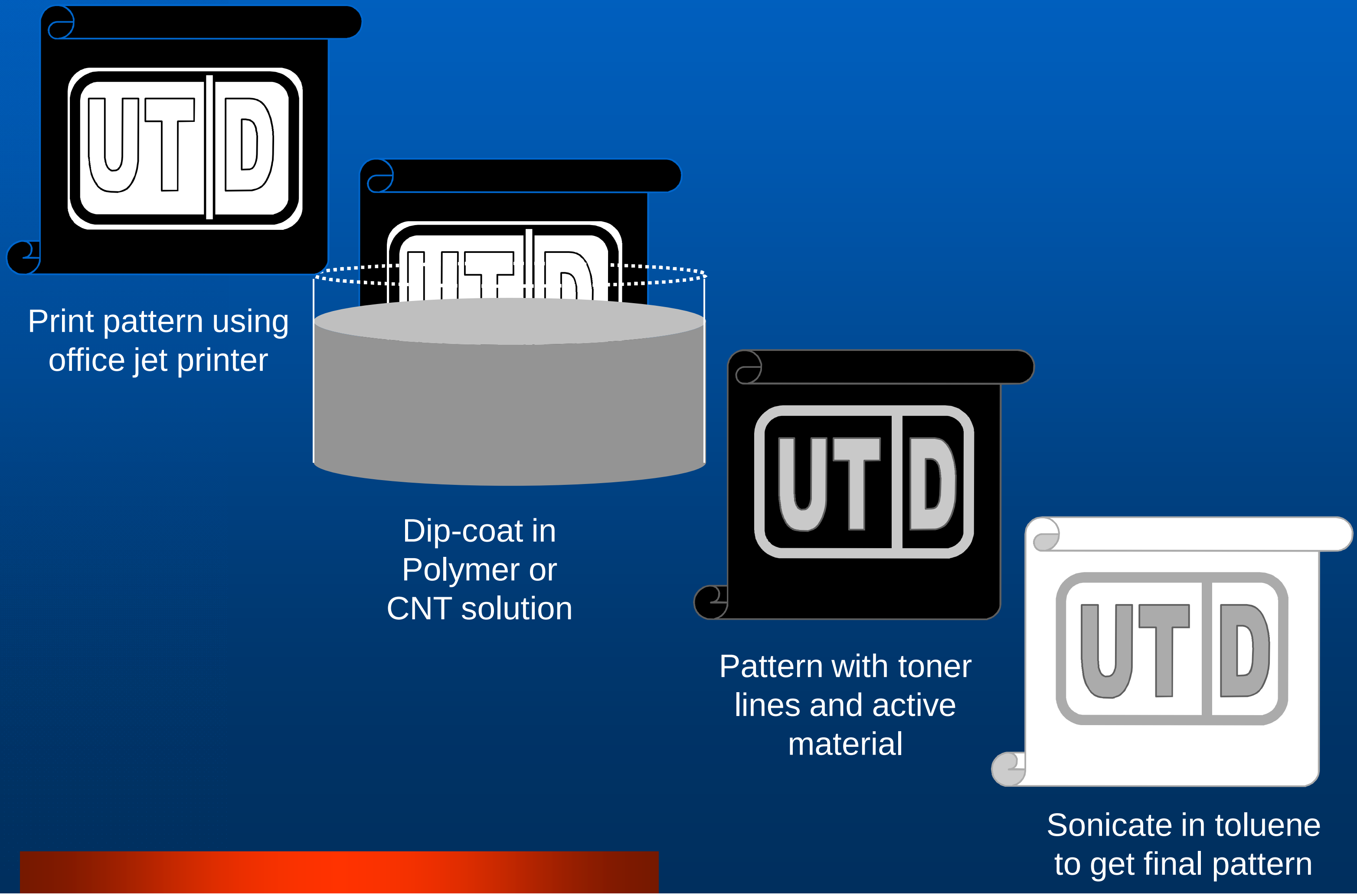

SCHOTT





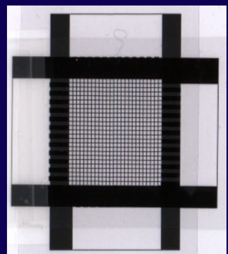


'Line Patterning' of Carbon Nanotubes (CNT) and Electronic Polymers

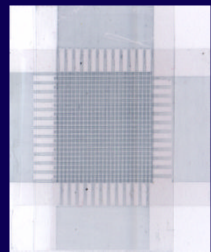


625 pixel PDLC* Liquid Crystal Display

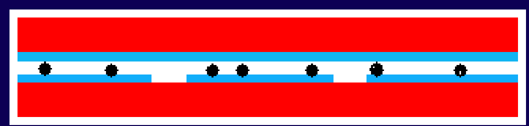
Make PEDOT conducting polymer pattern in usual way



Remove toner lines



~15mm polystyrene spherical spacers in PDLC



Transparency

Patterned PEDOT coating

Transparency

** Conventional <u>P</u>olymer <u>D</u>ispersed <u>L</u>iquid <u>C</u>rystal*

FIELD EFFECT TRANSISTORS (FETs)

- *Completely inorganic (many papers)*
- *Hybrid : Si and Electronic Polymers (several papers since 1987)*
- *Completely Organic (3 papers since 1994)*

Garnier et al., (Science, 1994)
deLeeuw, et al., (App. Phys. Lett. 2000)
Friend et al., (Science, 2000)

Using non-doped (semiconducting electronic polymers)

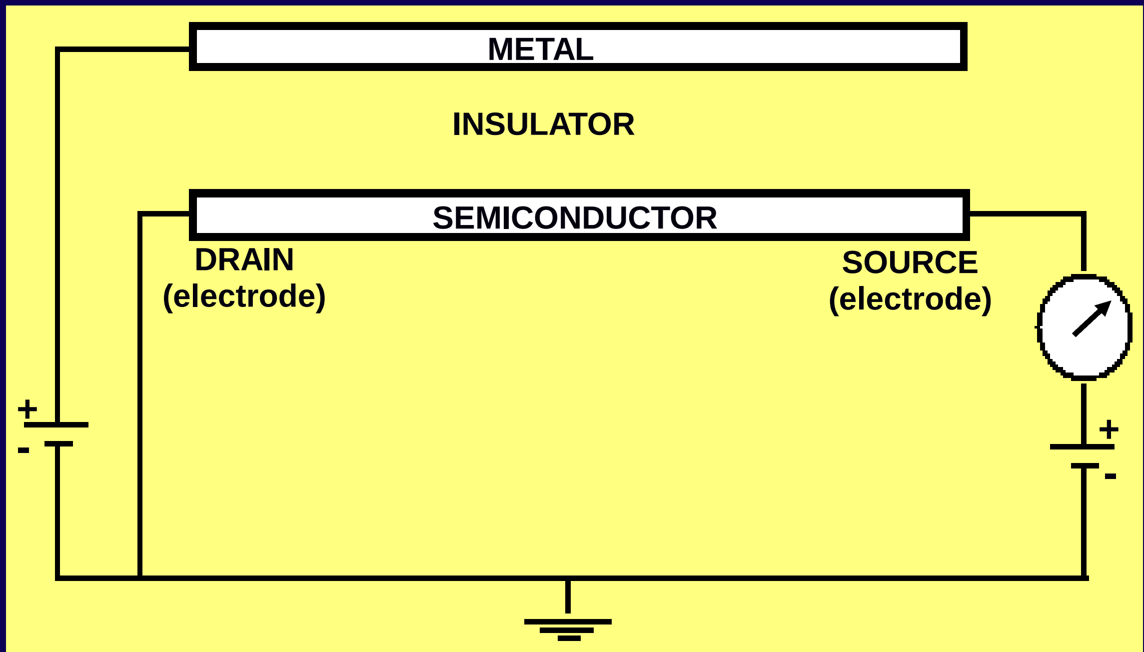
Field Effect Transistor

(i.e., a FET, a schematic)

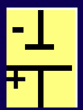
Gate connected to <u>only one terminal</u>

No current can flow between gate and circuit

Gate potential is with respect to ground



Positive Gate (V_G)



Negative Gate (V_G)

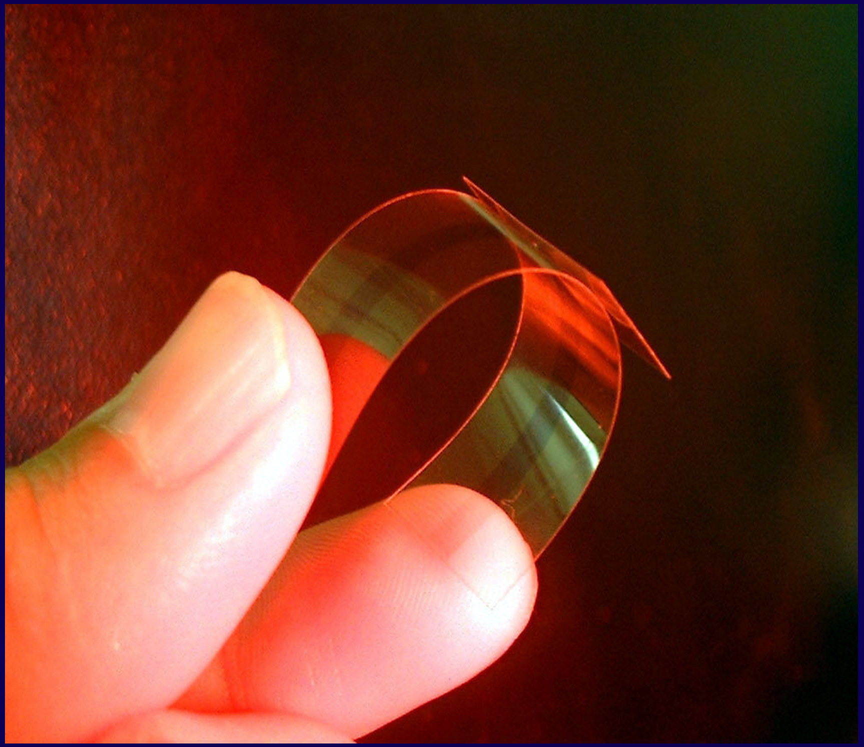
Source/Drain Current (I_{S-D})

Source/Drain Voltage (V_{S-D})

Not an Electrochemical effect- No current flows between Gate and <u>Source/Drain</u>, i.e. <u>semiconductor</u> electrodes.

Also no field effect is observed when the distance between the gate and Source/Drain electrode is too great

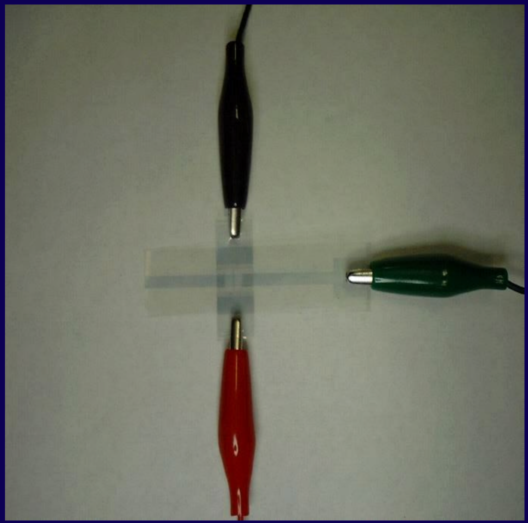
Plastic Transistor



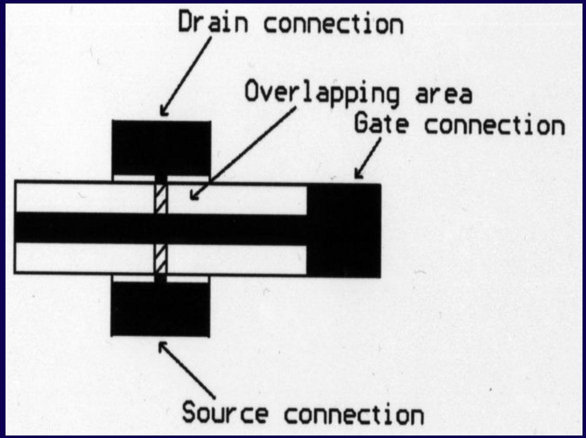
- All-polymer transistor
- Prepared by standard office printer in air by Line Patterning

H. Okuzaki et al., 2000

Field-Effect Transistor (FET)



FET transistor during operation



Schematic of FET assembly

- **Both "gate" and "source/drain" electrodes are "PEDOT" films on plastic sheets (by Line Patterning).**
- **Insulator is optical adhesive cement.**

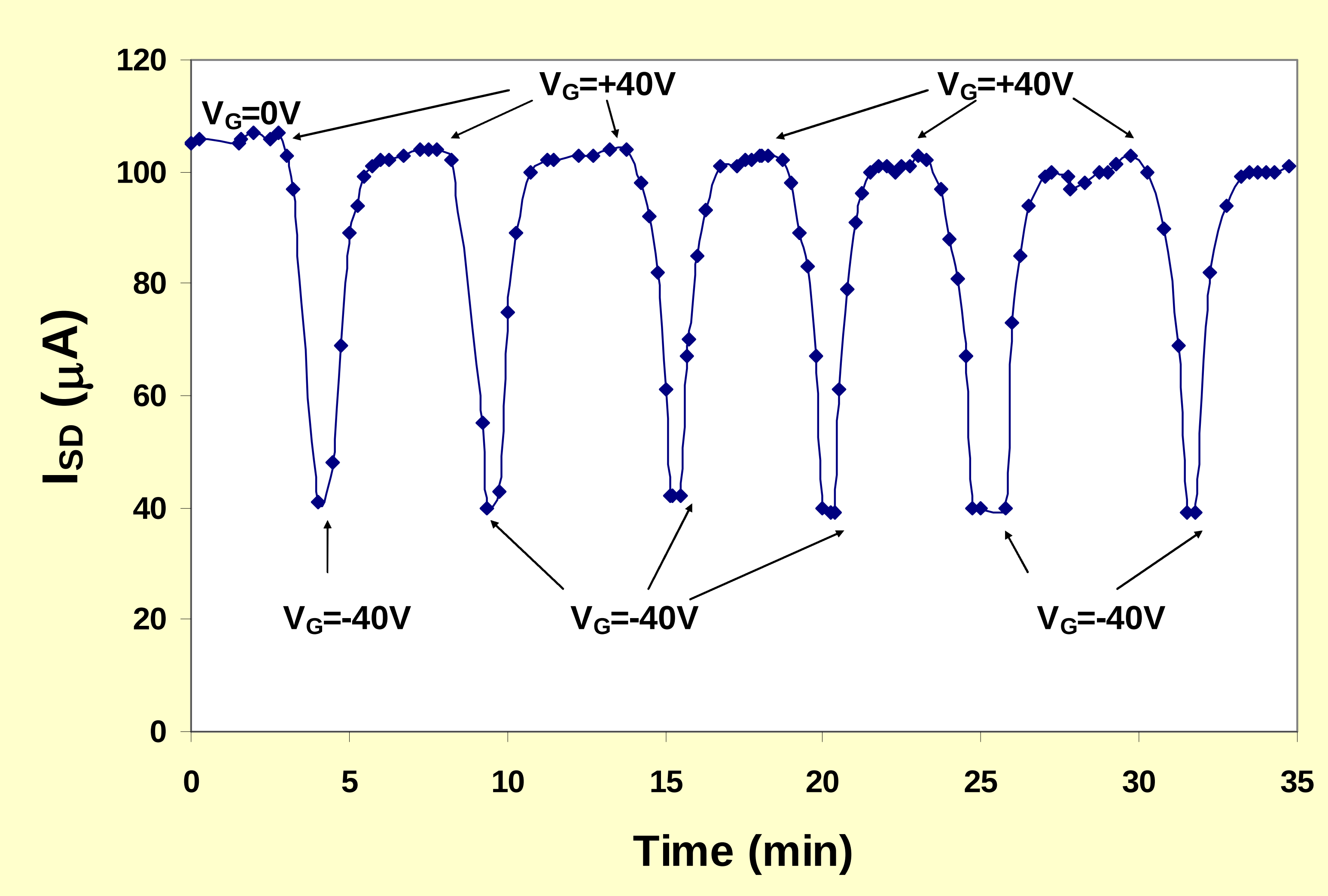
Field Effect with Doped Polyaniline

(Emeraldine.HCl by in situ deposition from Aqueous Solution)

(all components are organic)

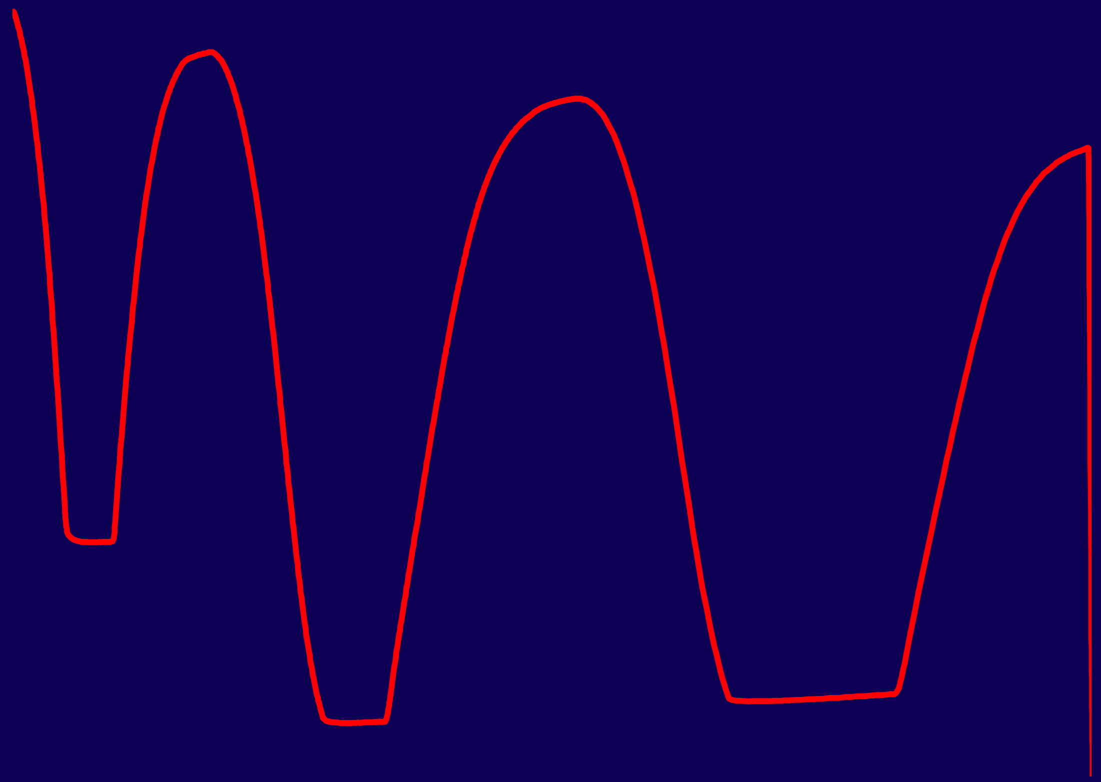
Doped Polyaniline (emeraldine. HCl)

A negative V_G reverses effect



Doped Polyaniline (emeraldine. HCl)

A negative V_G <u>reverses</u> effect

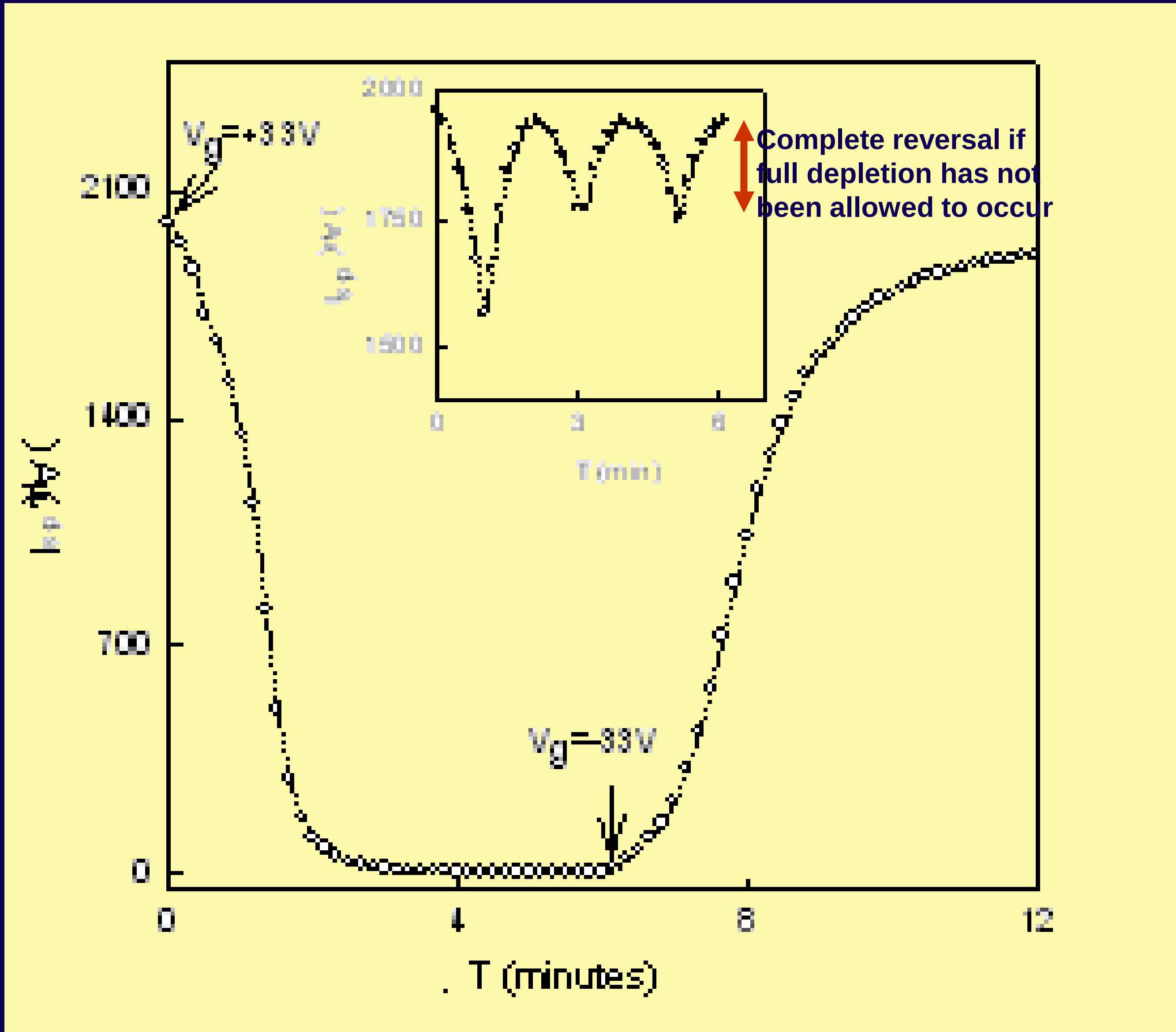


Polyaniline. HCl

2.1mA!!
V_{SD}=18V

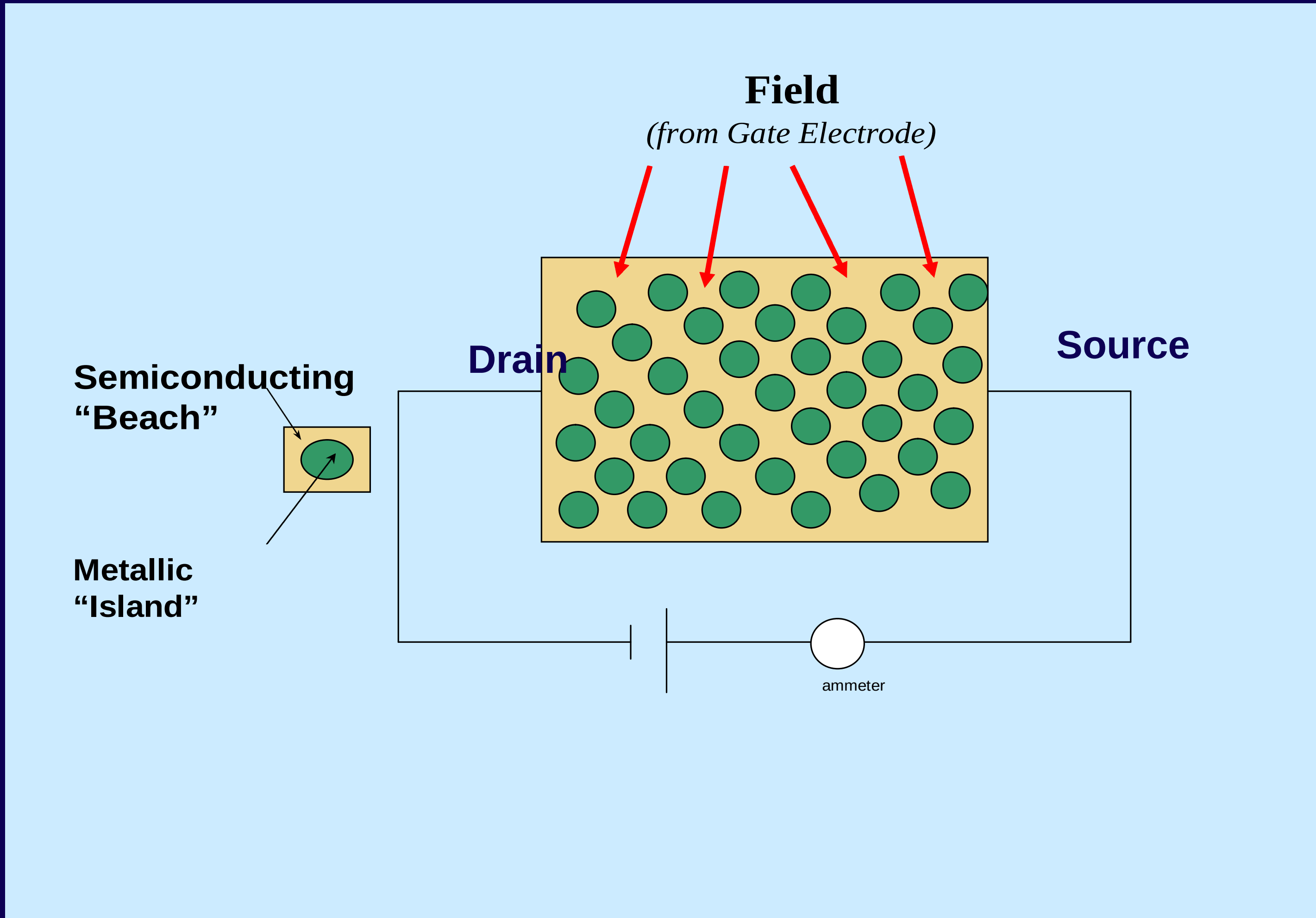
Note:
Commercial conventional Motorola transistor (#2N5457) has: a I_{SD} ~1mA At V_g =0Vand V_{SD}=18V

Note:
I_{SD} of all previous FETs using an electronic polymer are 10^3 to 10^6 smaller than this



Field Effect Mechanism…the Island Model

No field effect should occur with a metallic substance between the source/drain electrodes (σ of doped PEDOT and Polyaniline ~2S/cm)

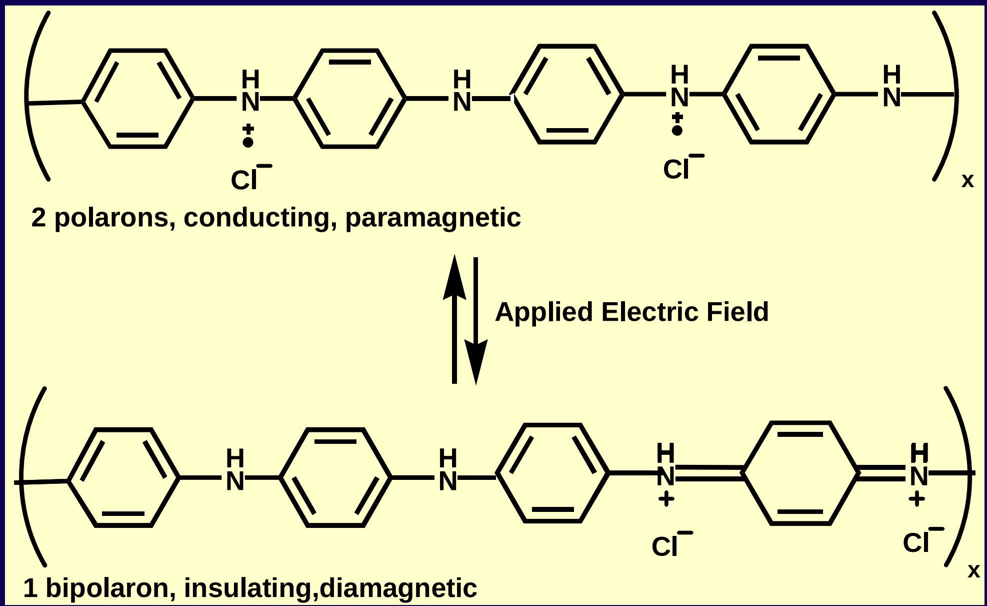


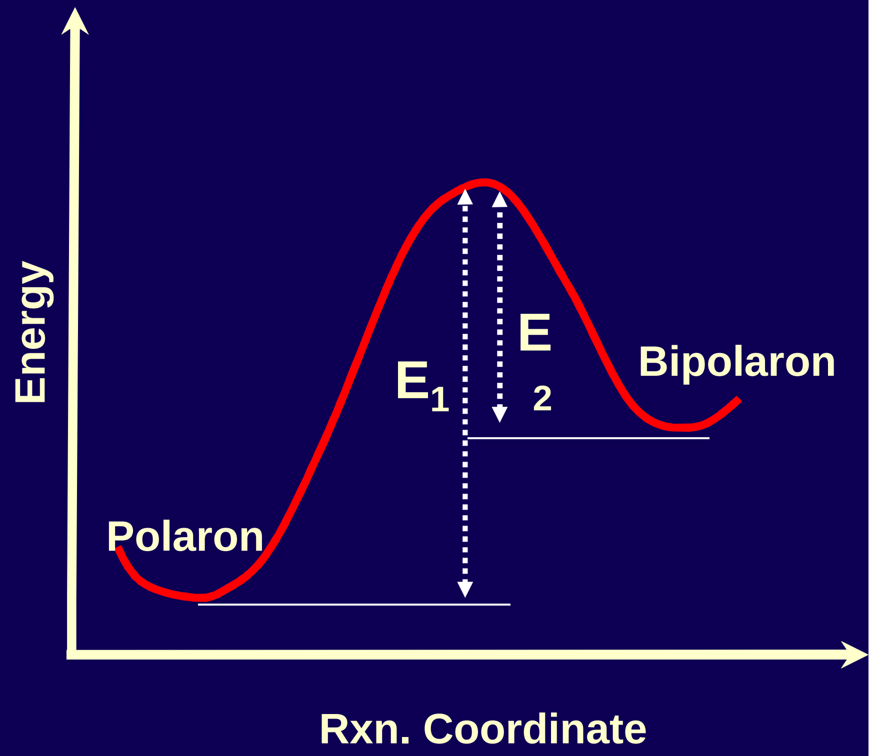
OR…..

Possibly, the field changes the conductivity of BOTH "beaches" and "islands" ???

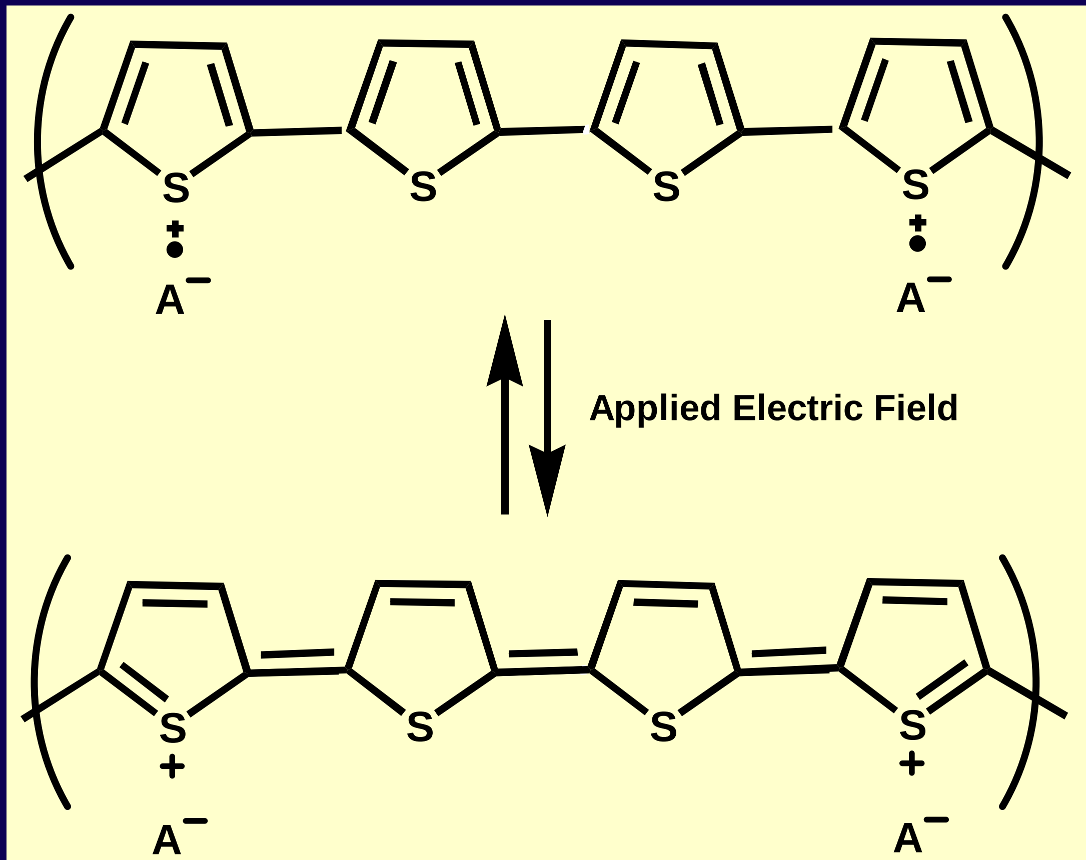
Polaron-bipolaron Equilibrium

Hypothesis: Application of either a positive or negative field promotes bipolaron formation





Polaron-bipolaron Equilibrium



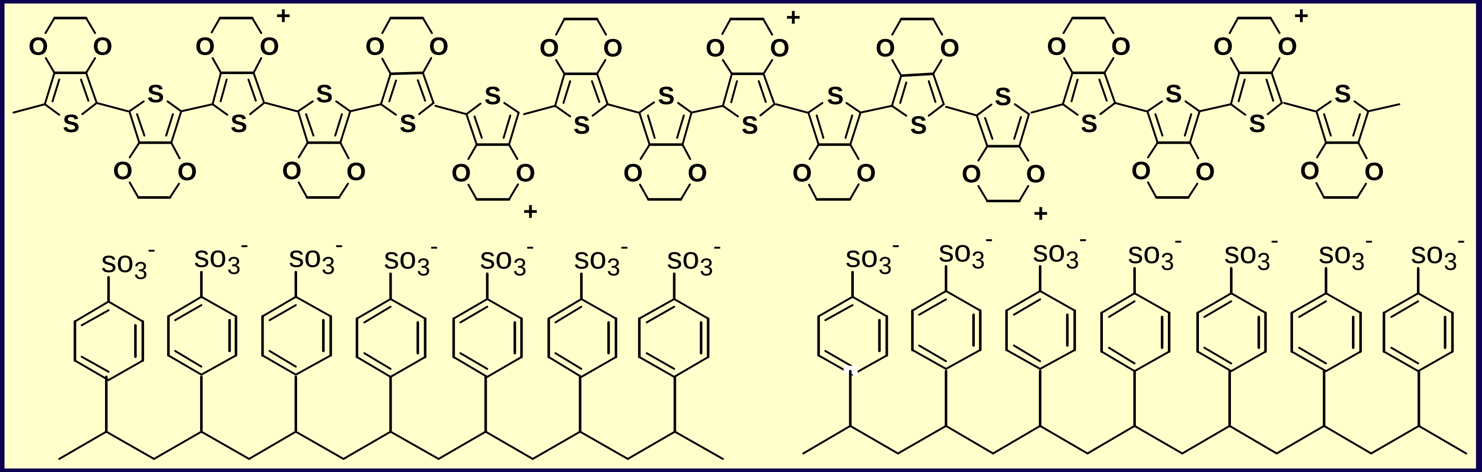
Sub-section Summary

- Line Patterning provides the potential for cheap, “throw-away” electronic circuits on plastic, paper and /or fabrics.
- A new electric field effect phenomenon is reported whereby the conductivity of a doped *metallic* polythiophene derivative and doped *metallic* polyaniline is changed many orders of magnitude by the application of a 10 – 40 volt gate potential.
- The much slower response time as compared to a conventional FET (employing semiconducting source/drain electrodes) suggests that (dopant) ion migration is involved, possibly related to polaron/bipolaron equilibrium.

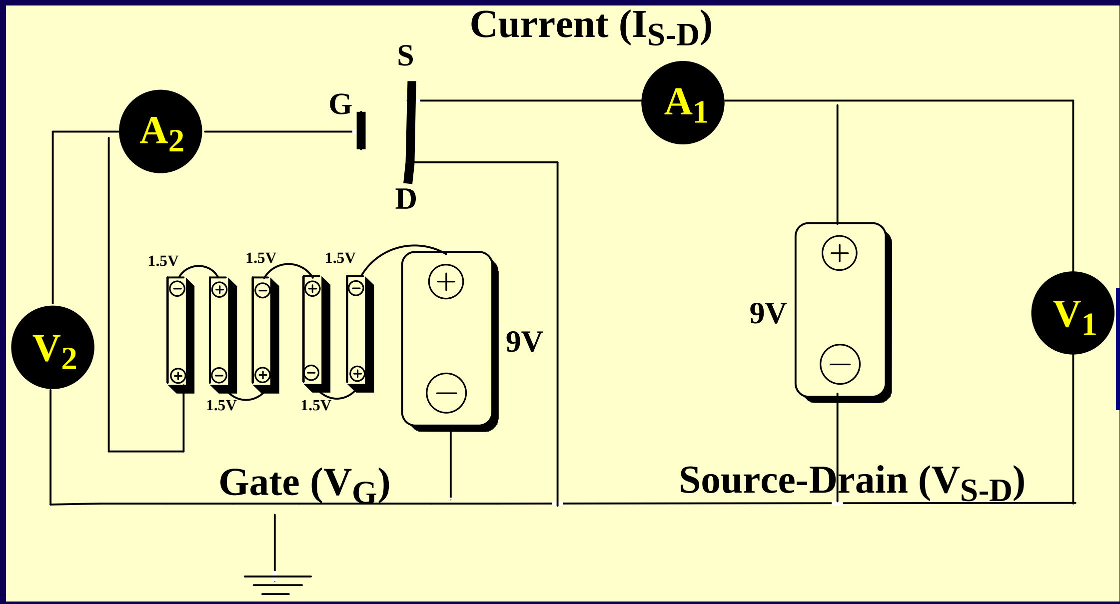
FIELD EFFECT WITH "PEDOT"

(all components are organic)

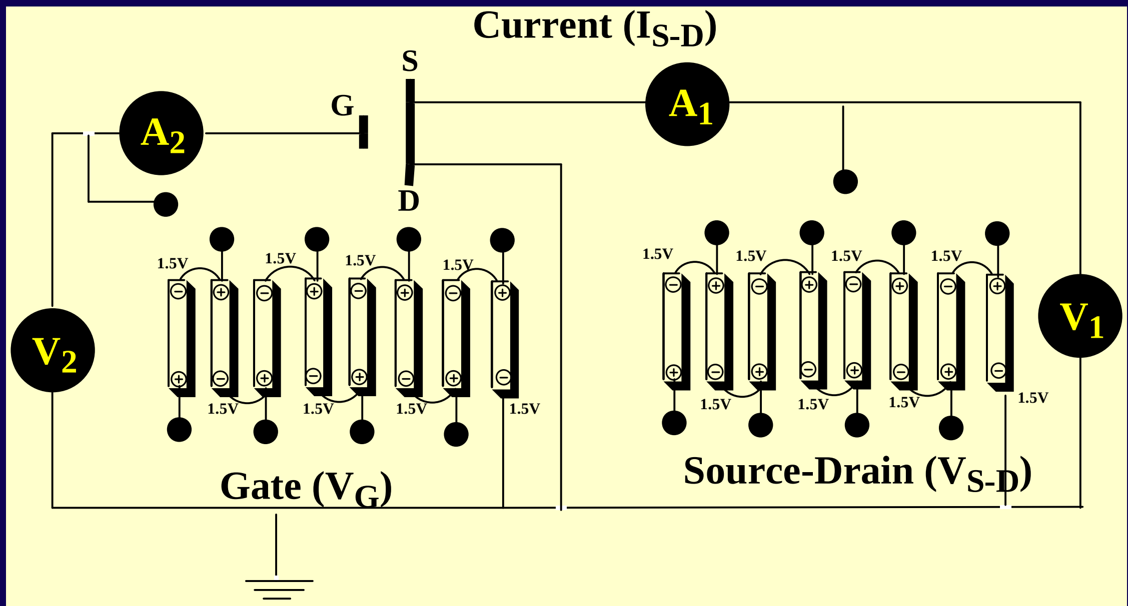
PEDOT



Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PSS) (BAYTRON P, Bayer Co. Pittsburgh, PA), concentration 1.3%w (~1:2.5 PEDOT:PSS); doping level ~1/3 ethylenedioxythiophene, EDOT); molecular weight of PSS 200,000; repeat units of EDOT 5-10 repeat units.

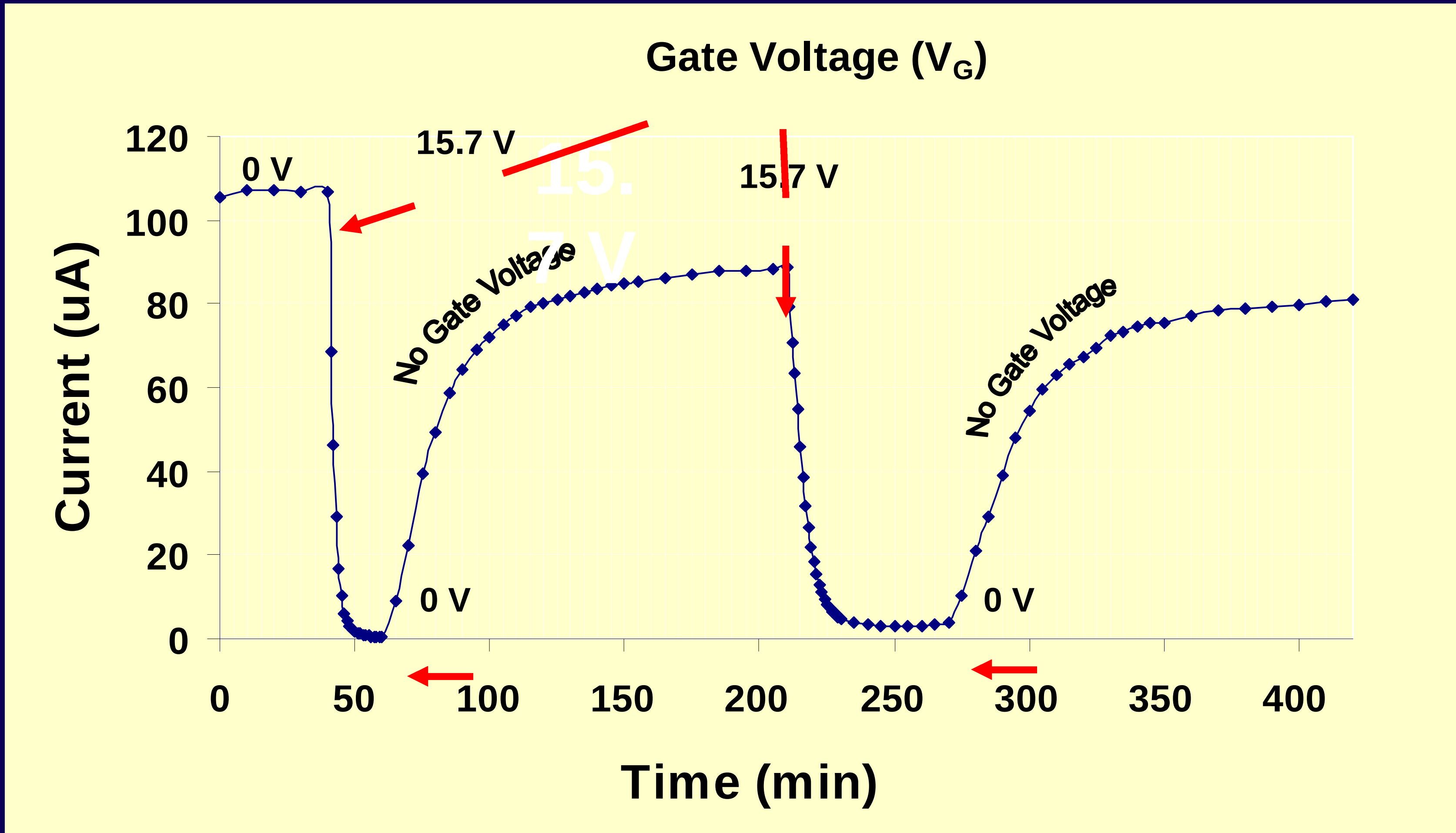


Constant G voltage ~15V
Constant S-D voltage ~9V



Variable positive G and S-D voltage ~1.5V, 3V, 4.5V, 6V, 7.5V, 9V, 10.5V and 12V

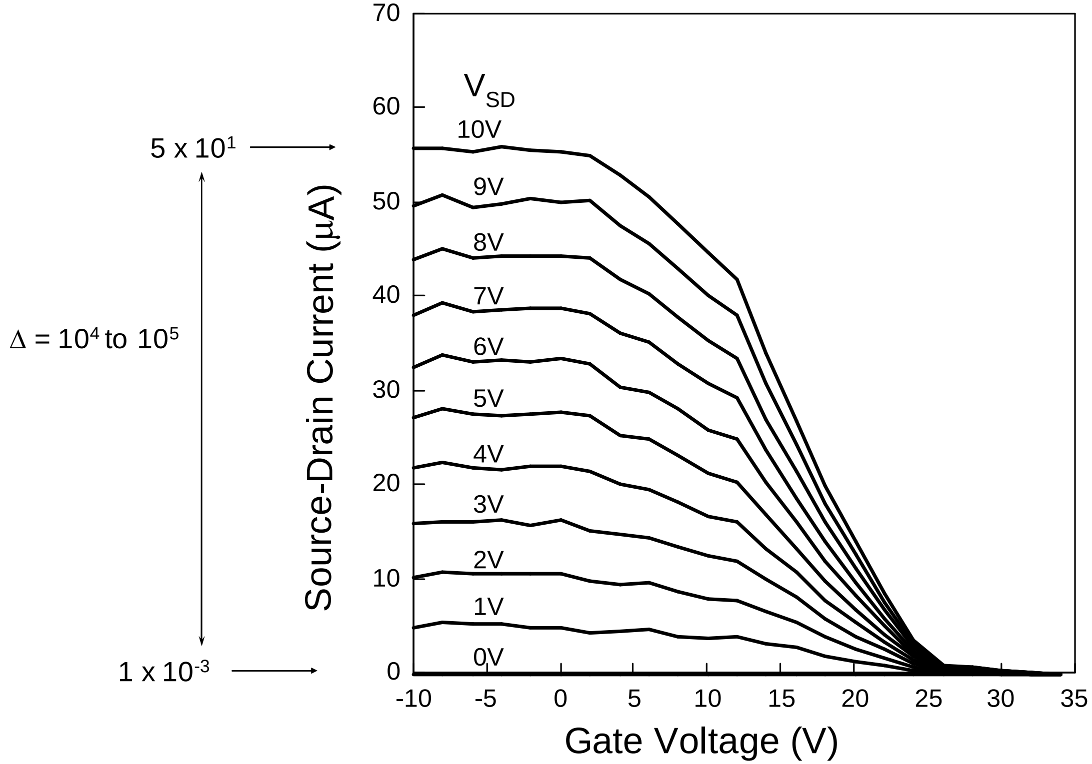
Field Effect in PEDOT



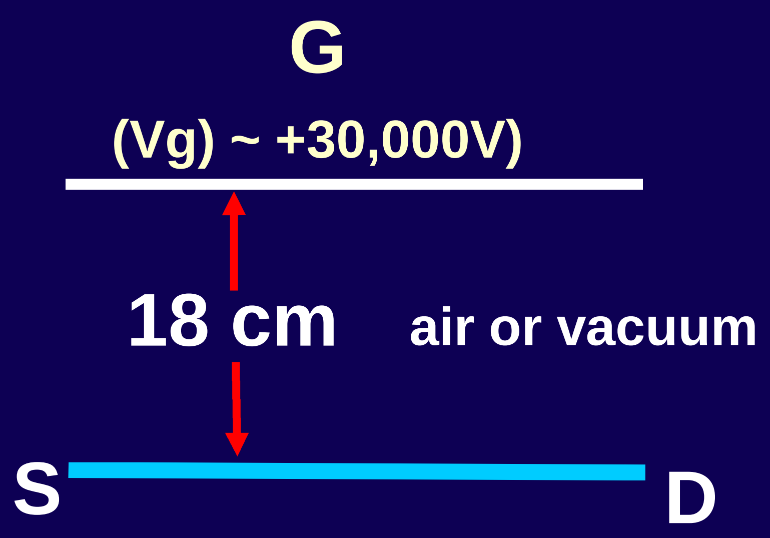
V_{SD} = 8.7V

FET Curves for PEDOT

“on” / “off” ratio



Field Effect Significant With PEDOT Film Source/Drain Electrode over ~18 cm in Air or Vacuum

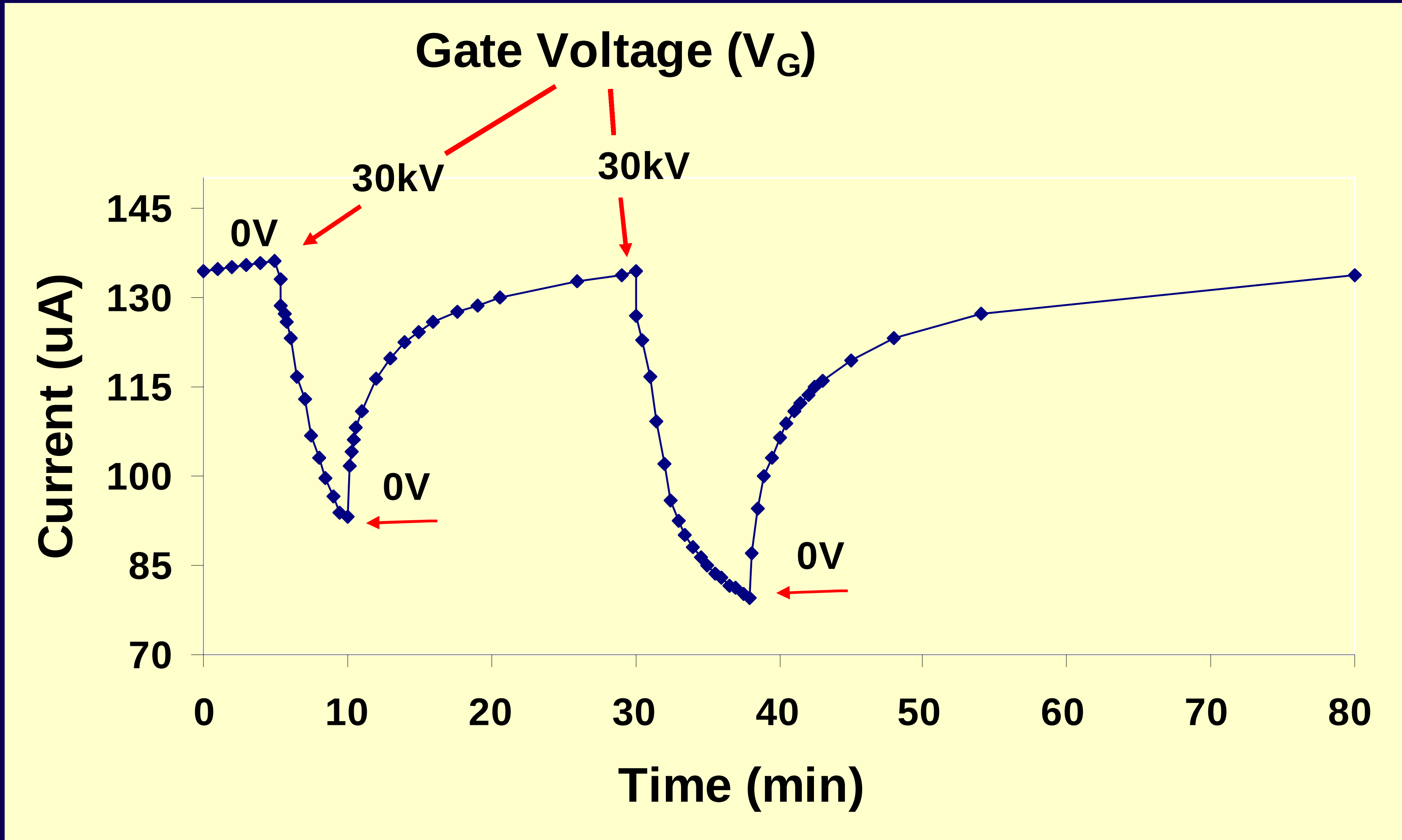


PEDOT Film (~80nm thick)

Electric Field: Volts/Distance = 1.67 x 10^5 V/m

<u>NOTE</u>: Electric Field Strengths for Previous Organic FETs Described above, ~10^7 V/m

Air as a Dielectric

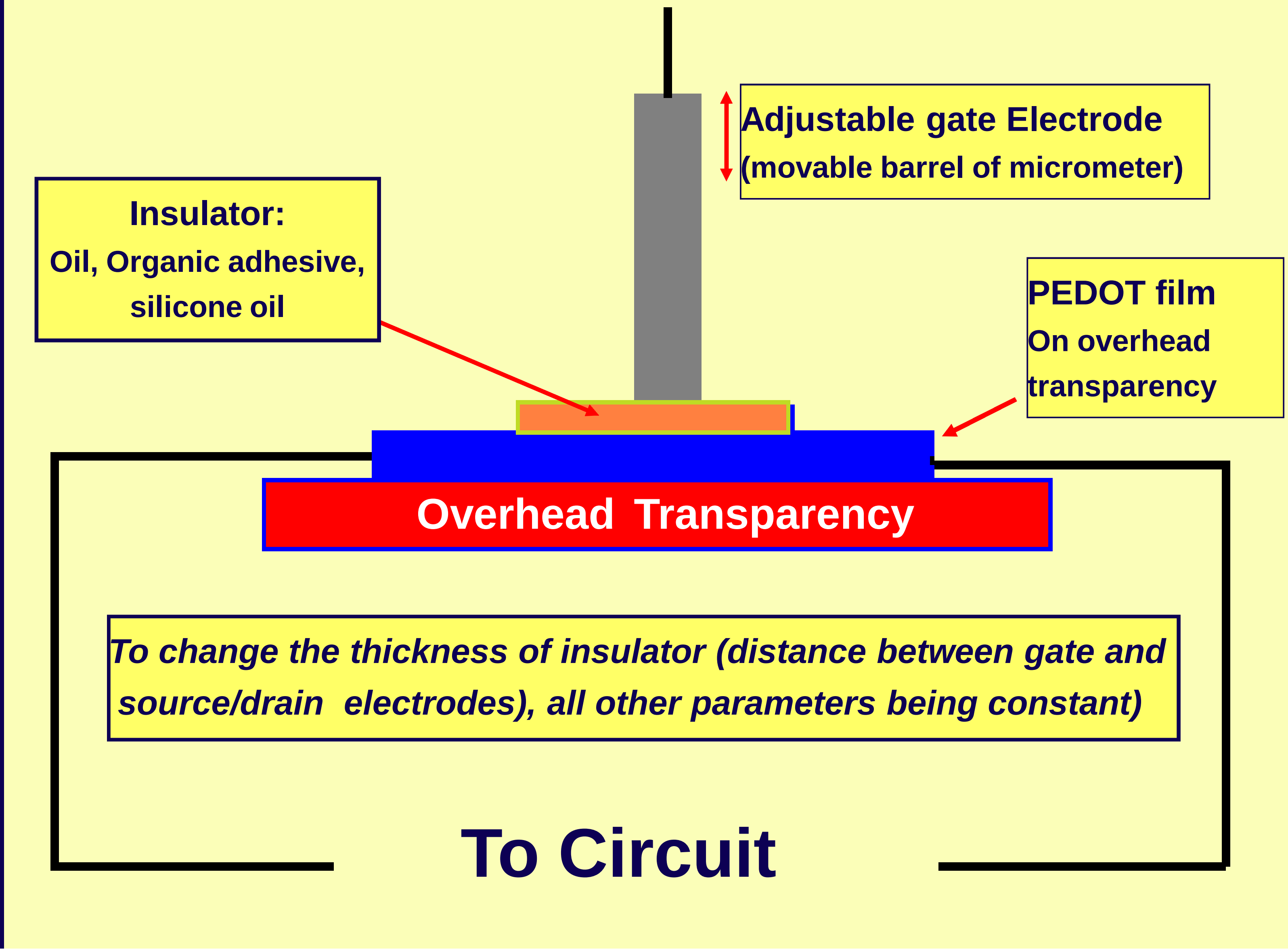


V_{SD} = 8.7V

$E = V/d$ = 30,000/0.065m = 4.6 x 10^5 V/m

PEDOT: 18cm air space (dielectric) between gate and source/drain PEDOT electrode

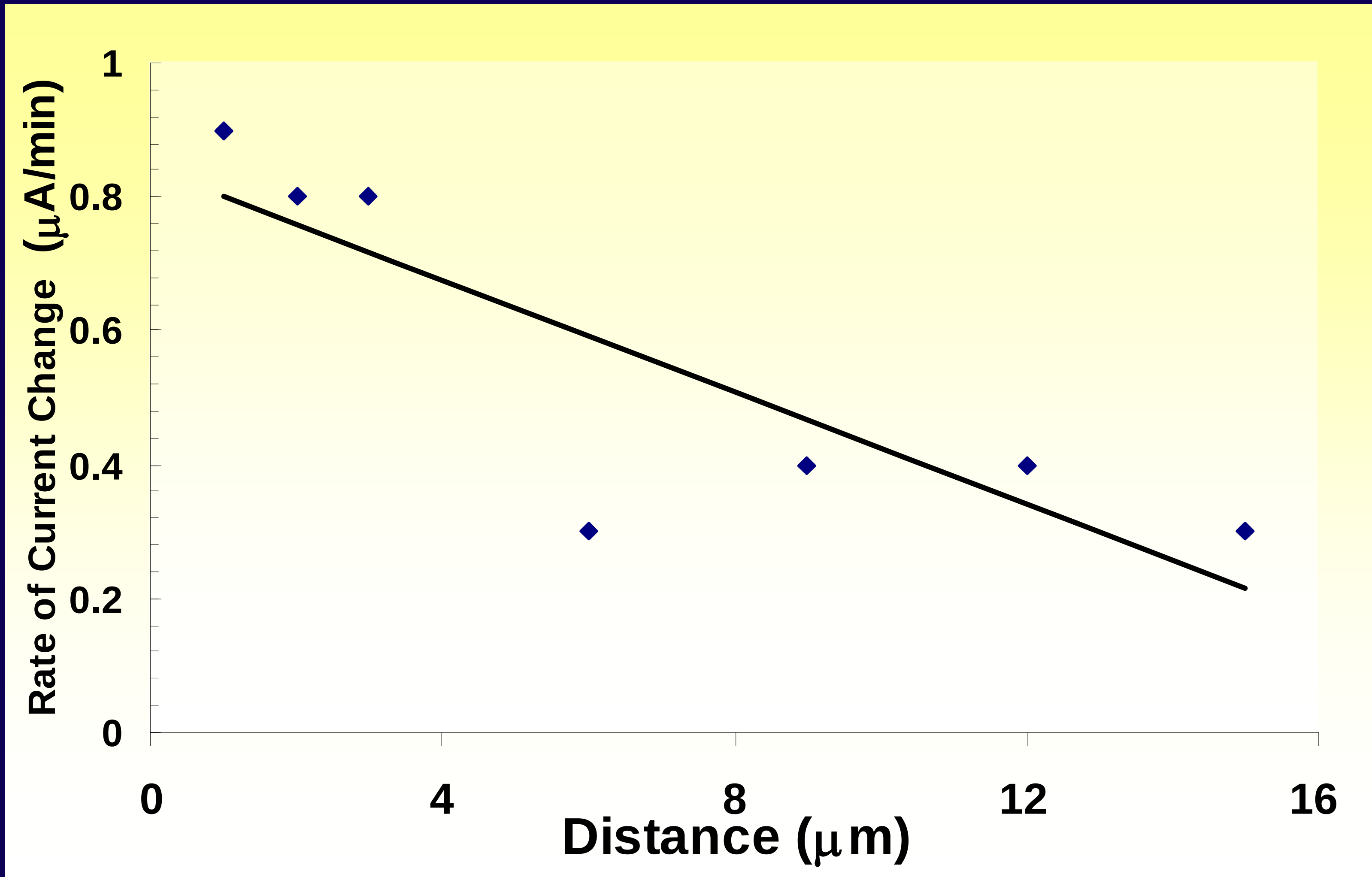
FET with Adjustable Gate Electrode



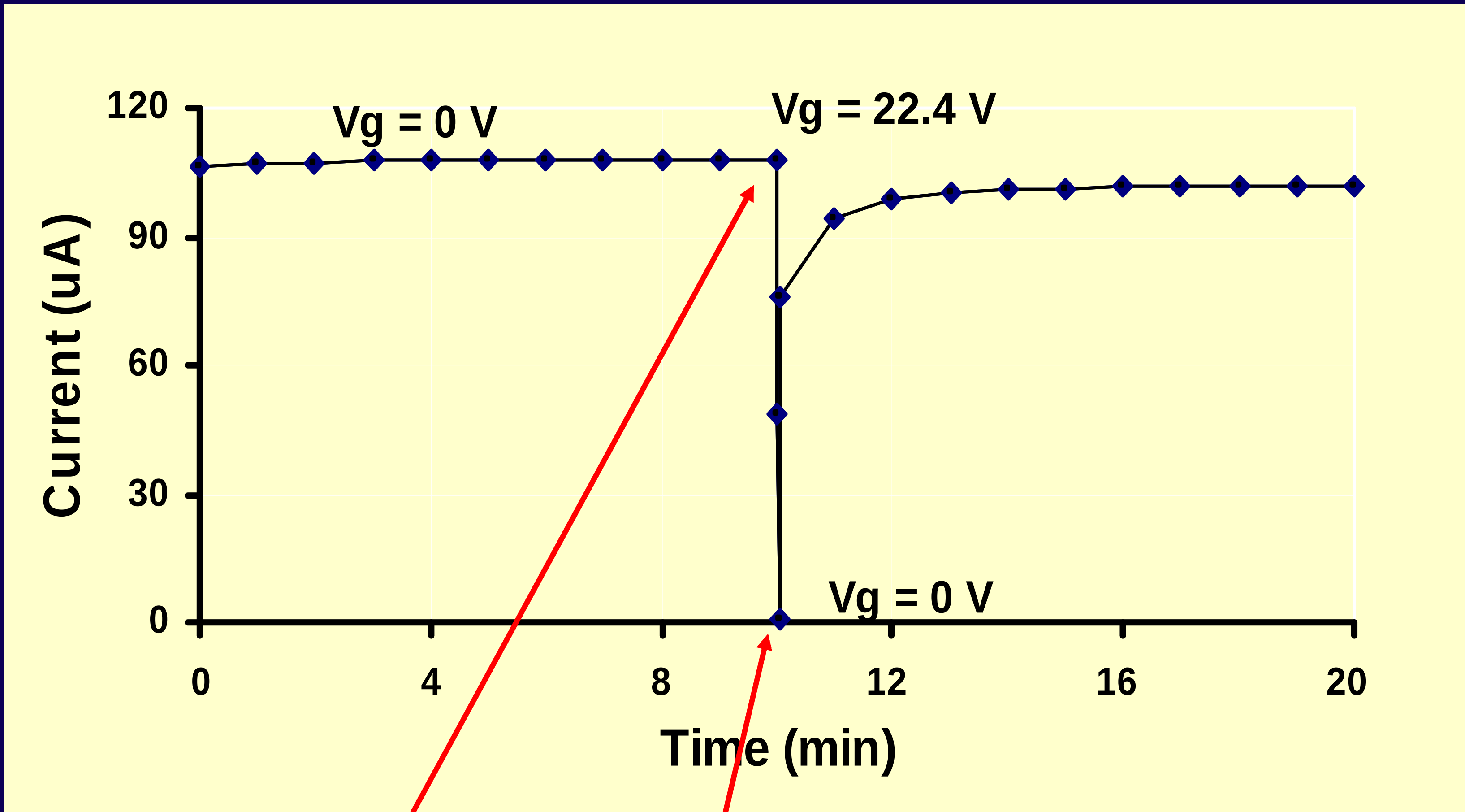
To change the thickness of insulator (distance between gate and source/drain electrodes), all other parameters being constant)

PEDOT: Effect of Distance

Vary only distance between gate & source/ drain electrodes. All other parameters held constant (V_{SD} = 8.7V; V_G = 22.4V



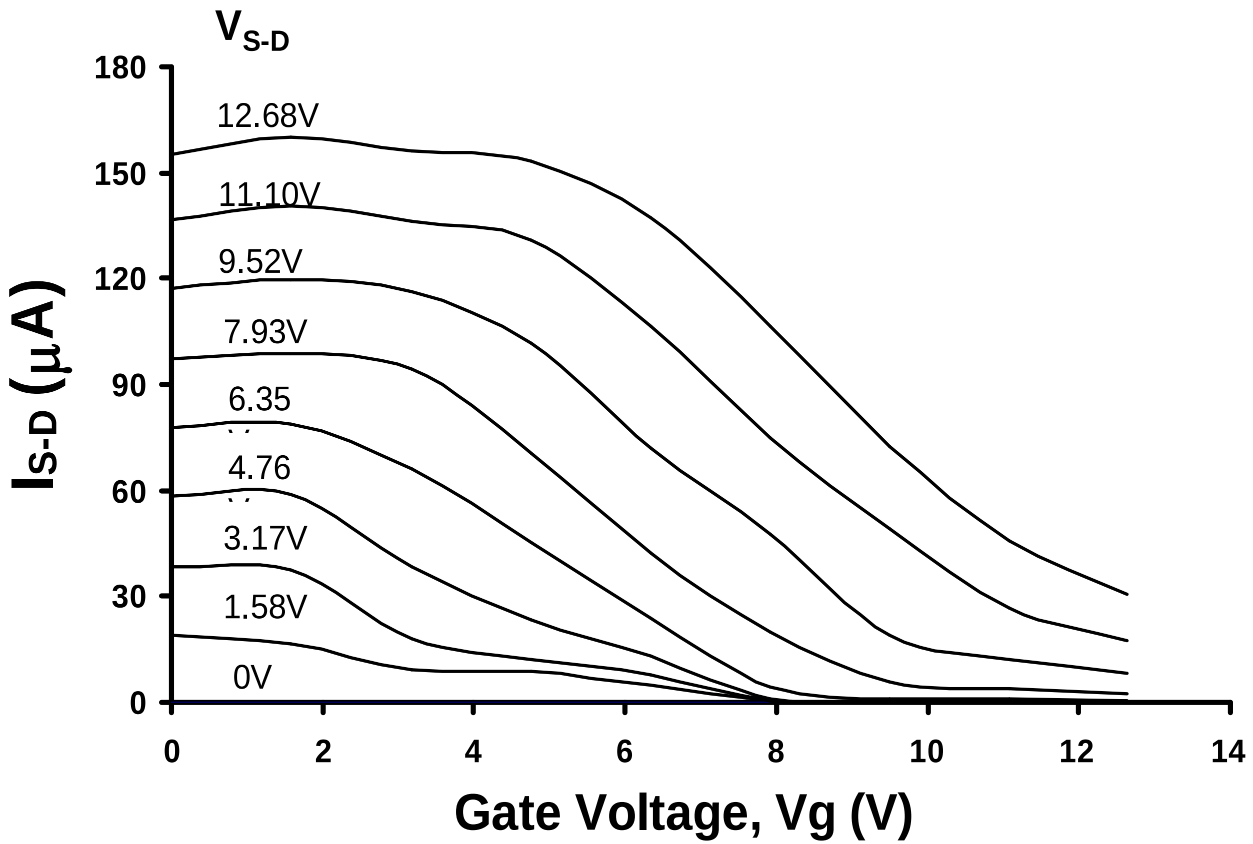
2-Second Response Time in PEDOT



- V_G changed to +22.4V (V_{SD}=8.7V)
- After ~2secs, V_G changed back to 0V

Insulator= silicone oil

Thickness of insulating layer = ~1μm



PEDOT Transistor

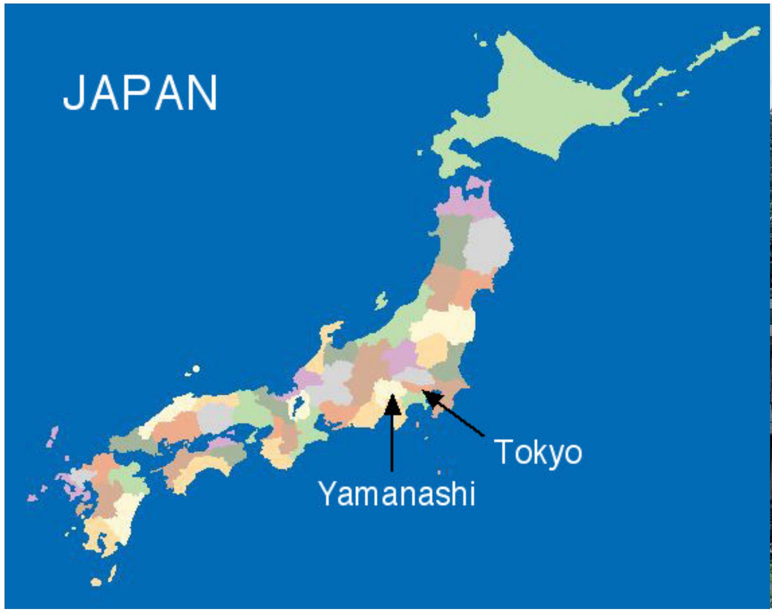
("Doped" ("metallic") PEDOT Gate and Channel

Doped Polymer-Based Field Effect Transistors Fabricated by Line Patterning

Hidenori OKUZAKI

Department of Applied Chemistry & Biotechnology

Faculty of Engineering, University of Yamanashi, JAPAN



Contents

Fabrication of FETs by Line Patterning

using

Illustrator, *Adobe*

LBP-470 (1200dpi), *Canon*

Transparency film (PET, 100μm), *Coop*

Baytron P (PEDOT/PSS), *Bayer*

Baytron P (Bayer Co. Ltd.)

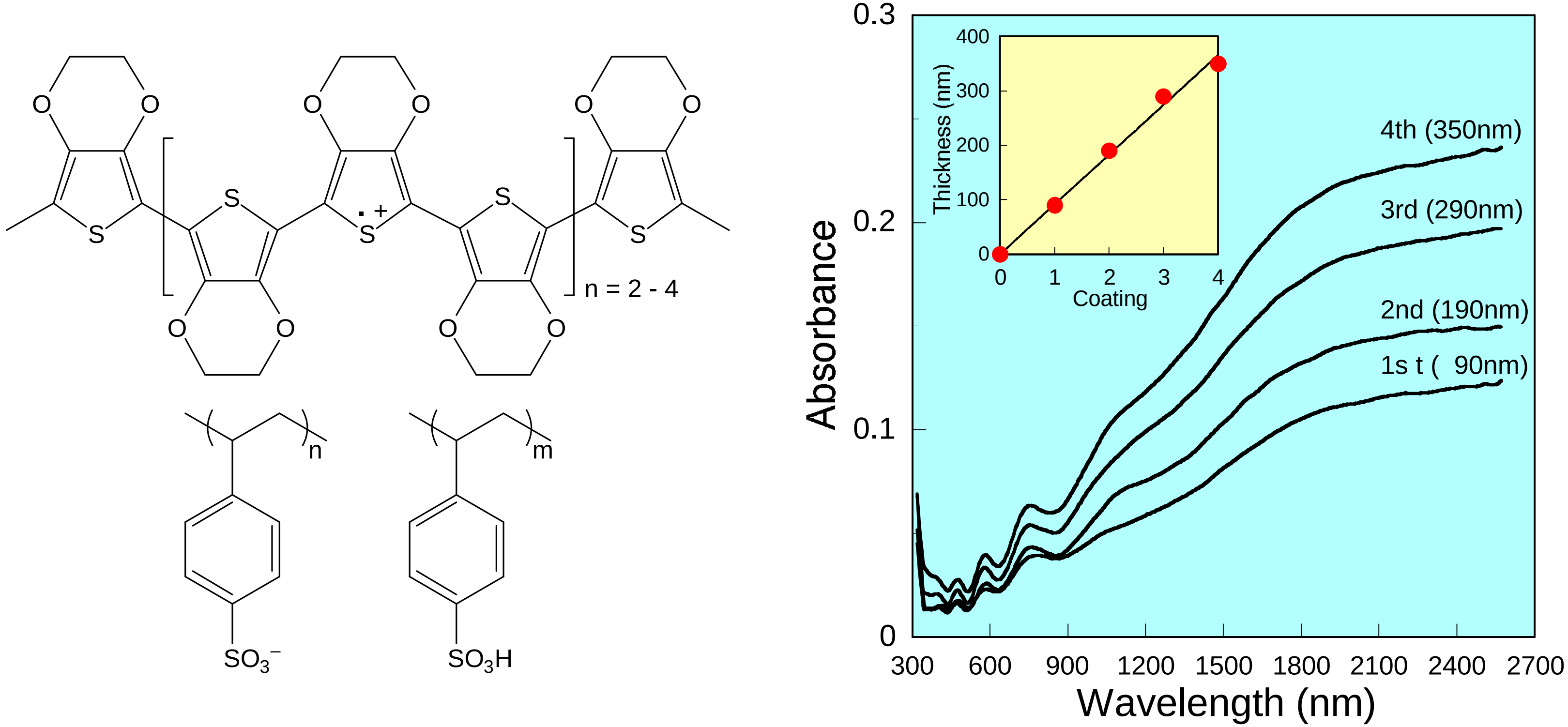
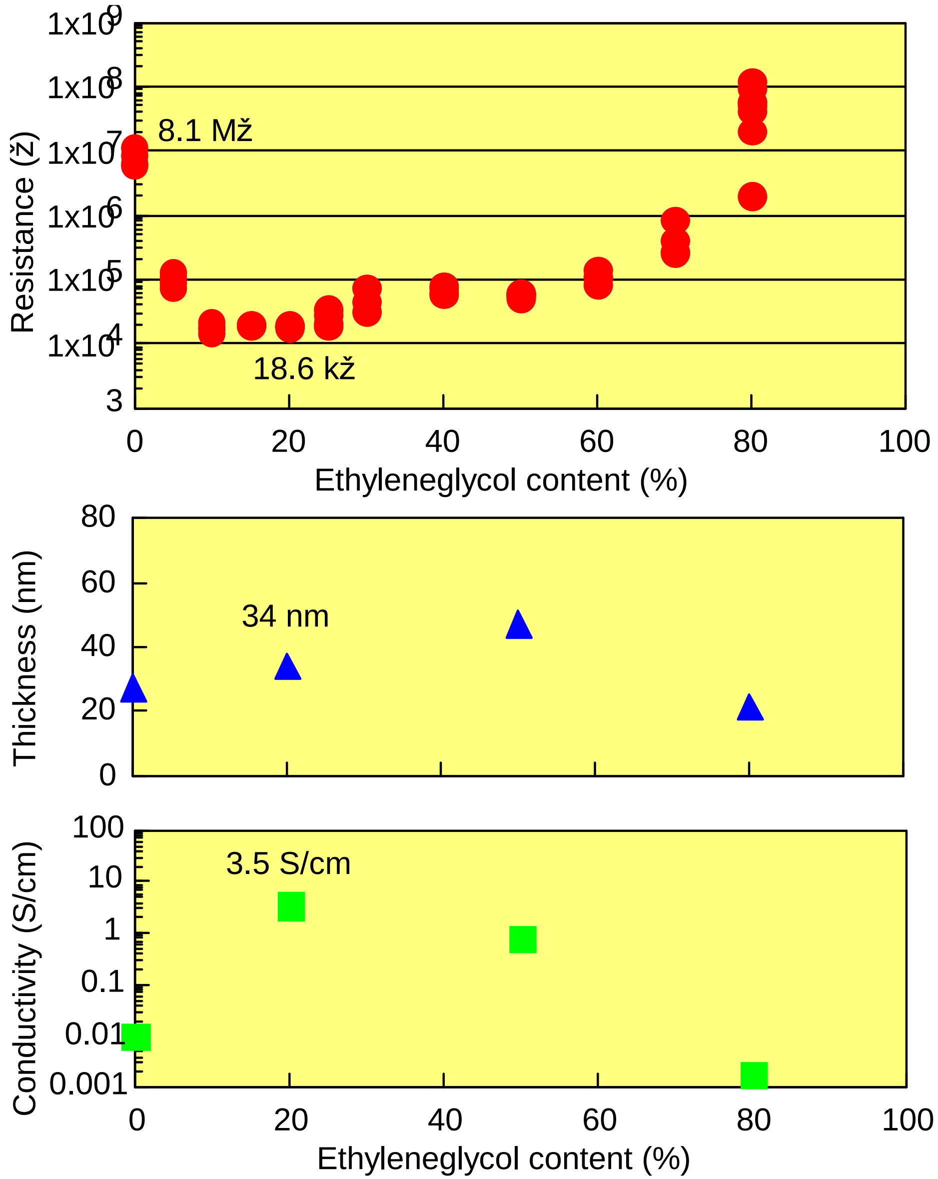
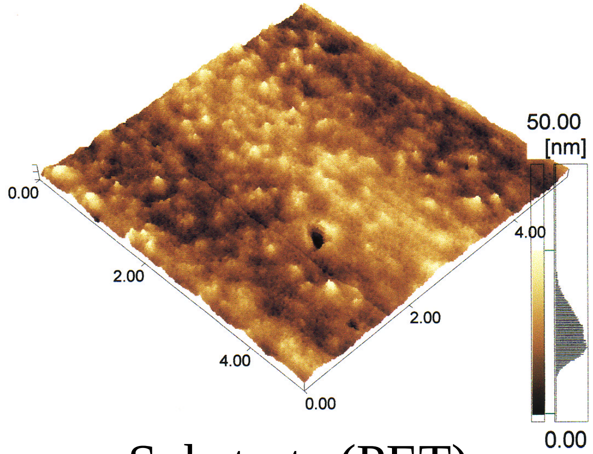


Fig. Chemical structure of poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT/PSS) and UV-Vis-NIR spectra of PEDOT/PSS coated on PET film.

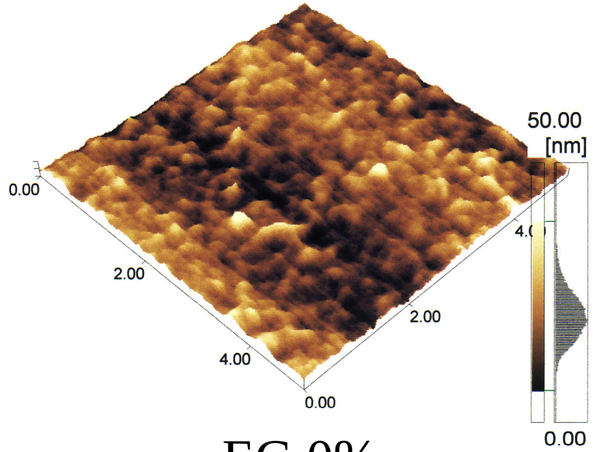
Effects of Elyleneglycol



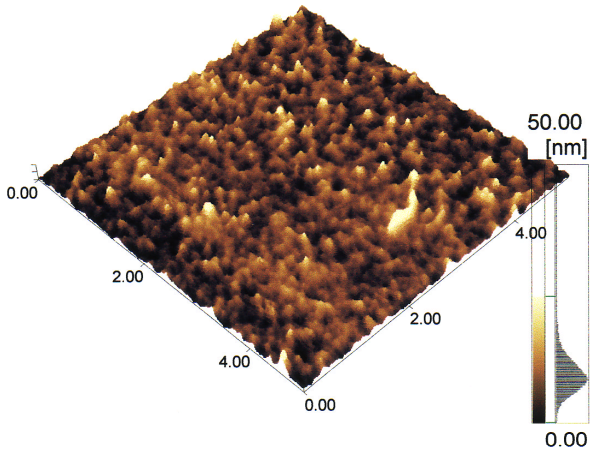
Surface Morphology



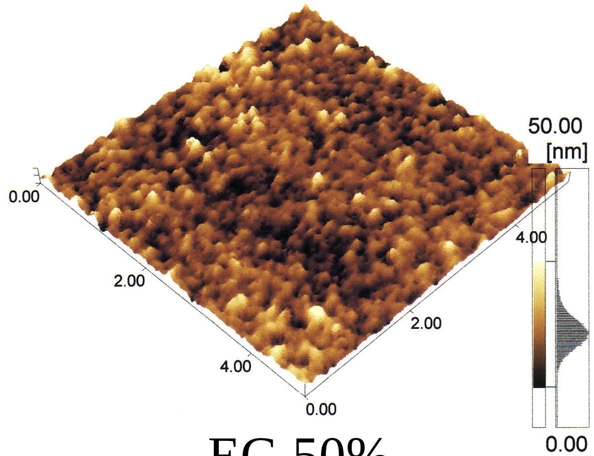
Substrate (PET)



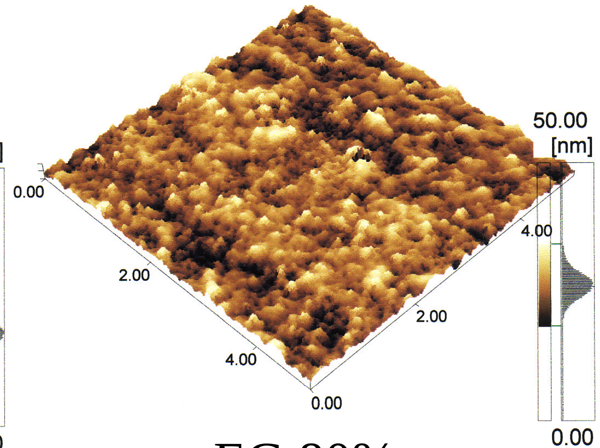
EG 0%



EG 20%

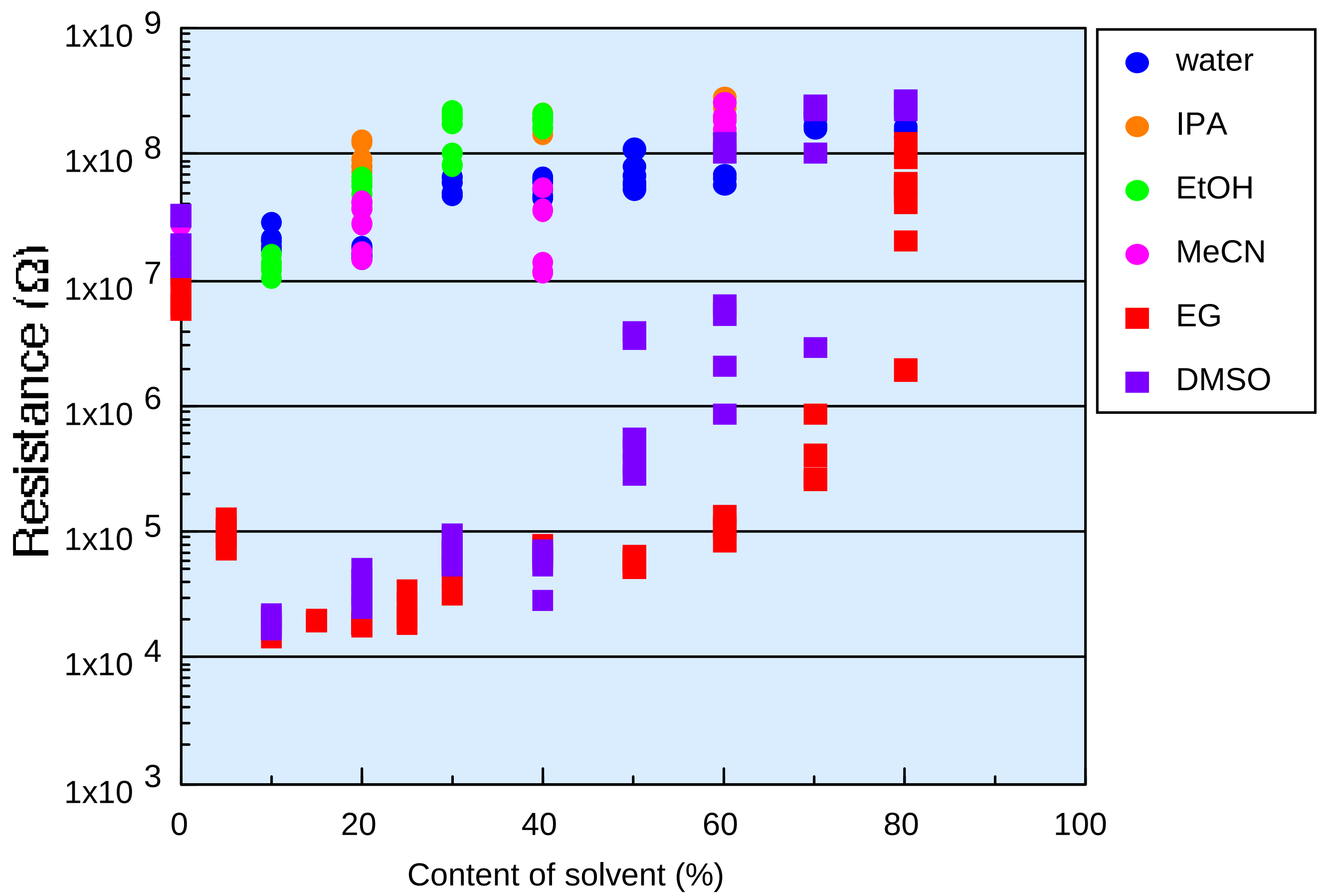


EG 50%

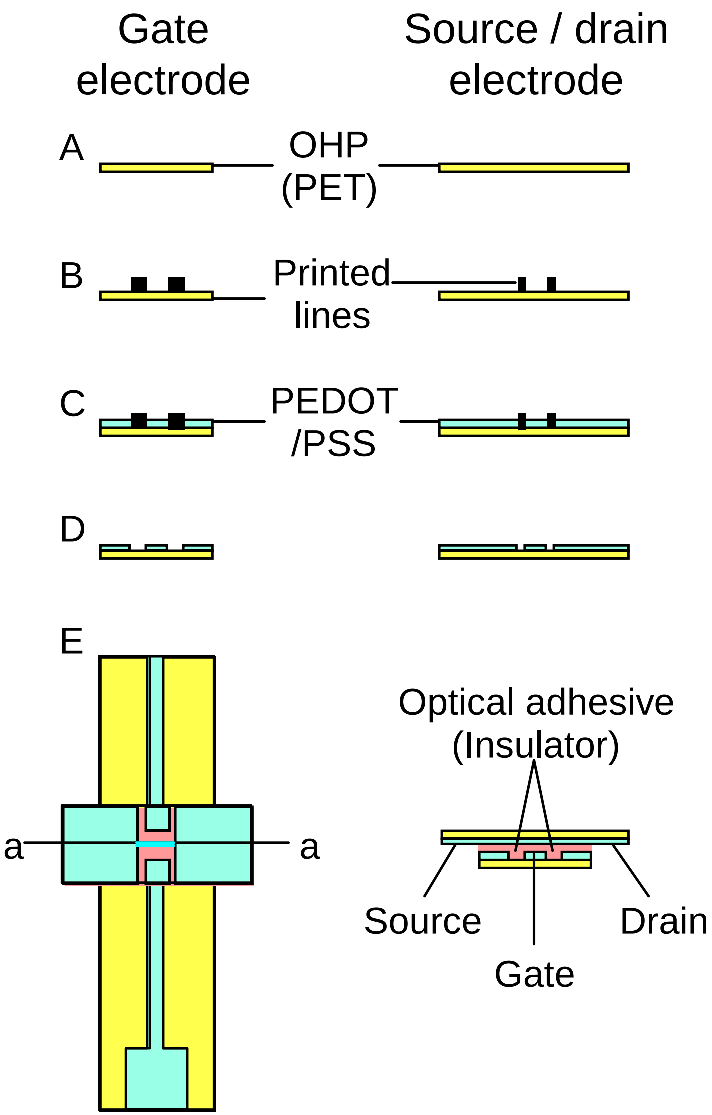


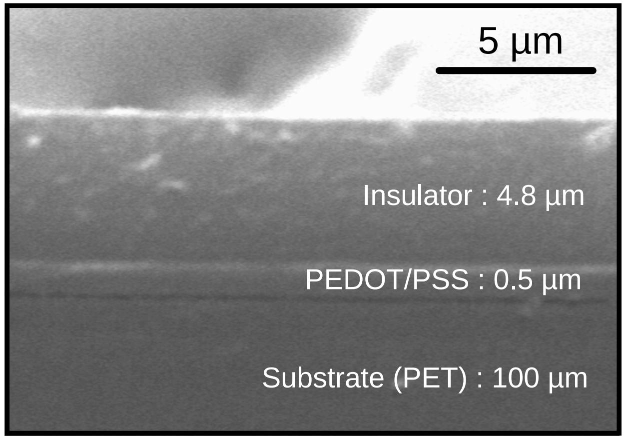
EG 80%

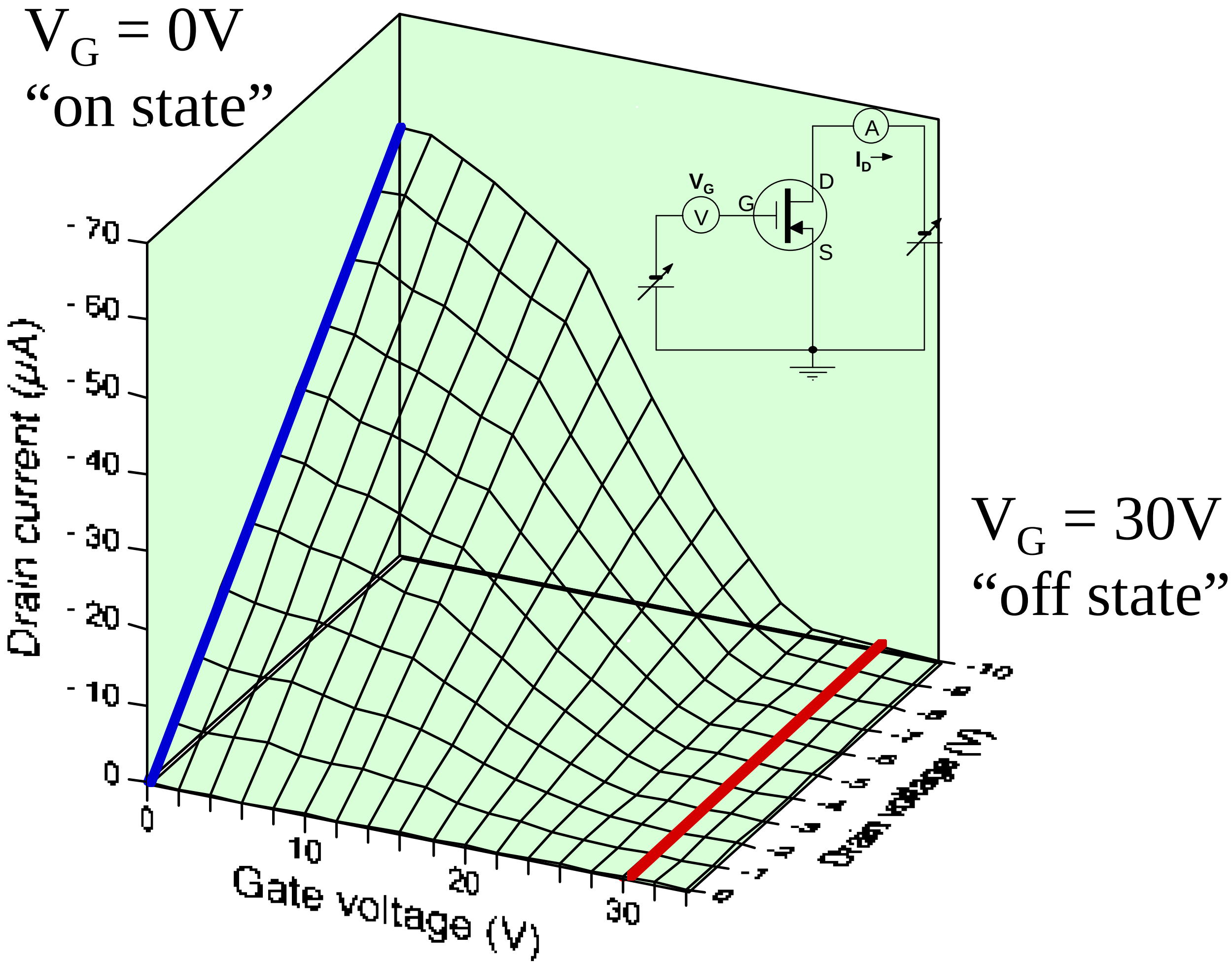
Other Solvents



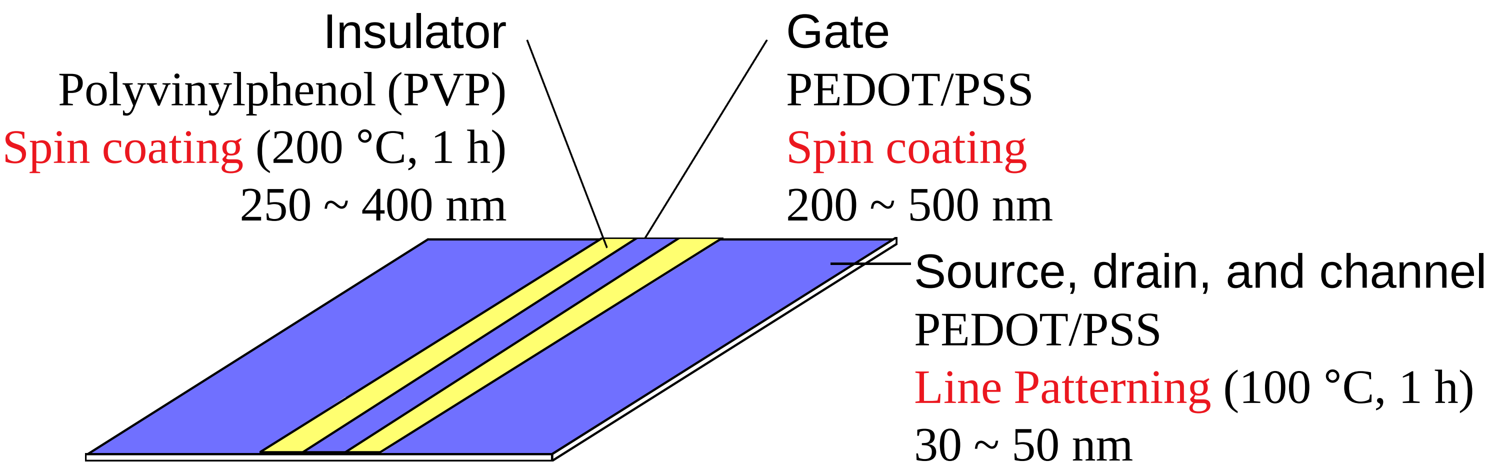
Field-Effect Transistor (FET)

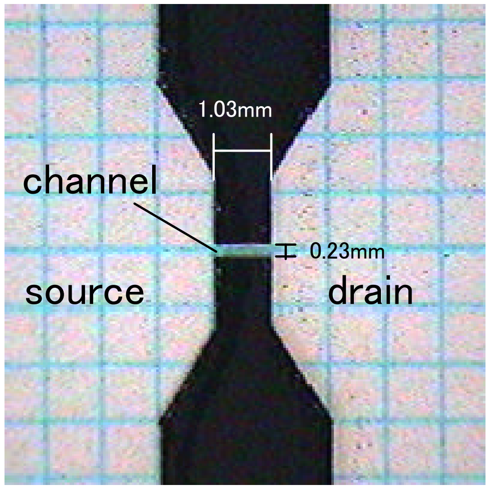


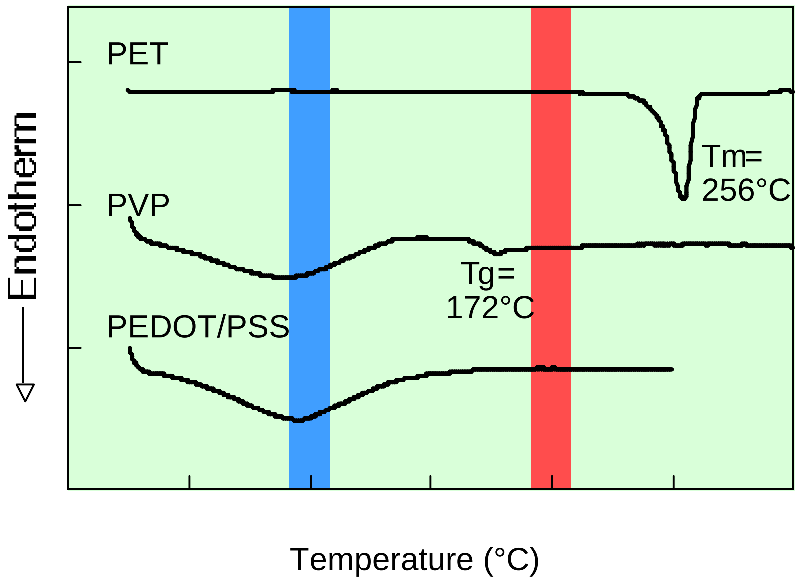




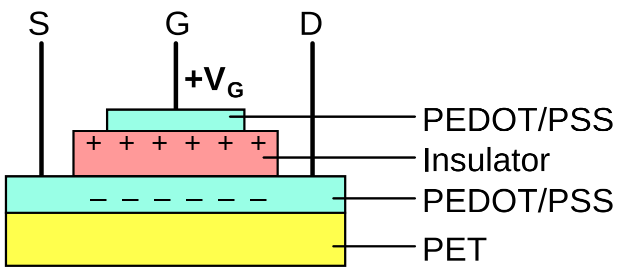
- High V_G is necessary
- Slow response (~ sec)
- Difficult to optimize the insulator

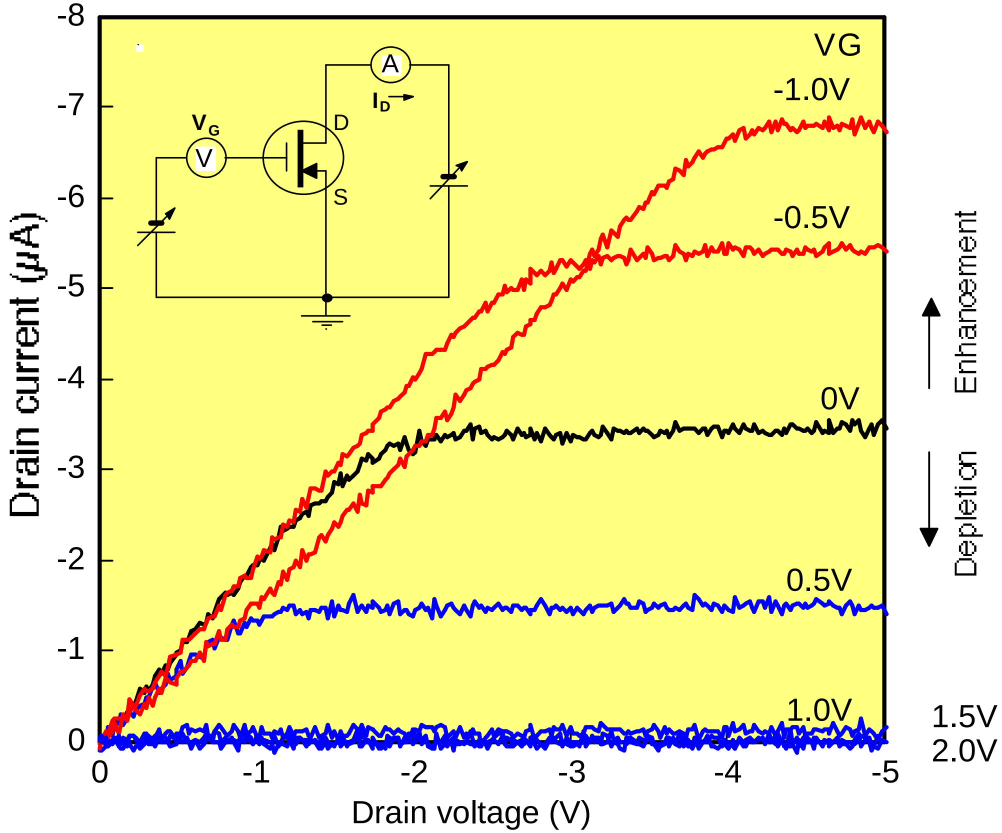

Insulator
Polyvinylphenol (PVP)
Spin coating (200 °C, 1 h)
250 ~ 400 nm
Gate
PEDOT/PSS
Spin coating
200 ~ 500 nm
Source, drain, and channel
PEDOT/PSS
Line Patterning (100 °C, 1 h)
30 ~ 50 nm


1.03mm
channel
0.23mm
source
drain

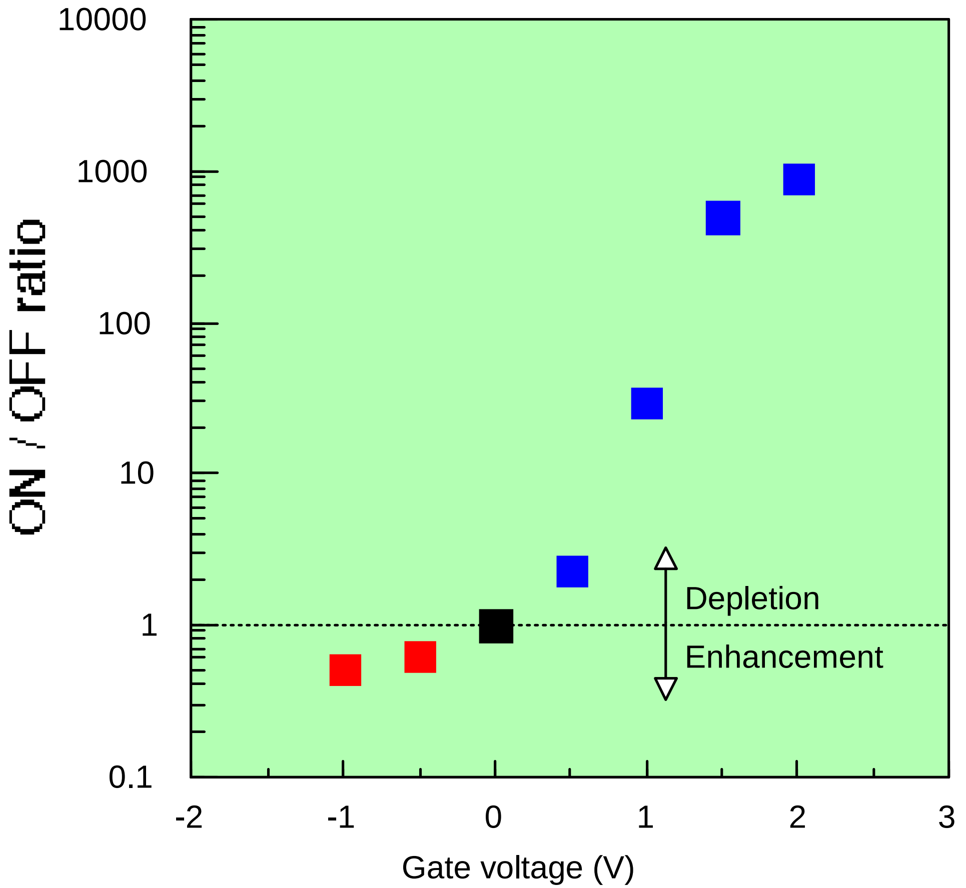

PET
Tm=
256°C
PVP
Tg=
172°C
PEDOT/PSS
Endotherm
Temperature (°C)

I-V Characteristics





ON / OFF ratio



ON / OFF ratio
10000
1000
100
10
1
0.1
-2
-1
0
1
2
3
Gate voltage (V)
Depletion
Enhancement

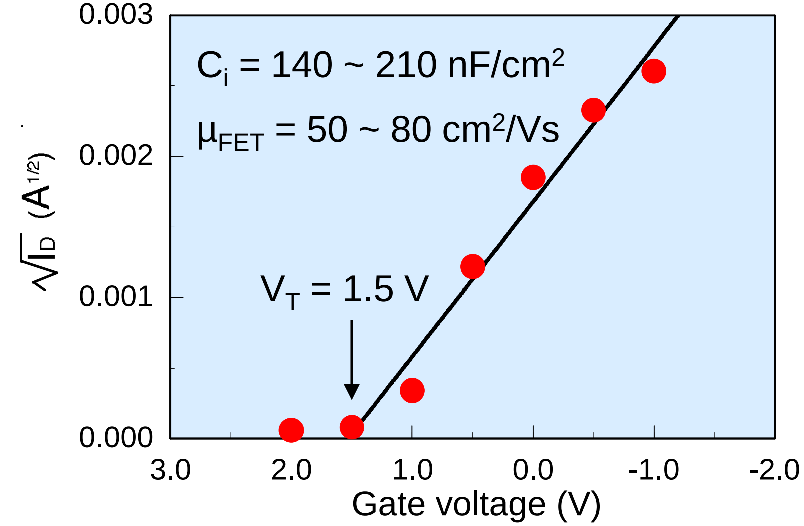
FET Mobility

$$I_D = \frac{WC_i}{2L}\mu_{FET}(V_G - V_T)^2$$

C_i : capacitance of the insulating area (nF/cm^2)

V_T : threshold voltage (V)

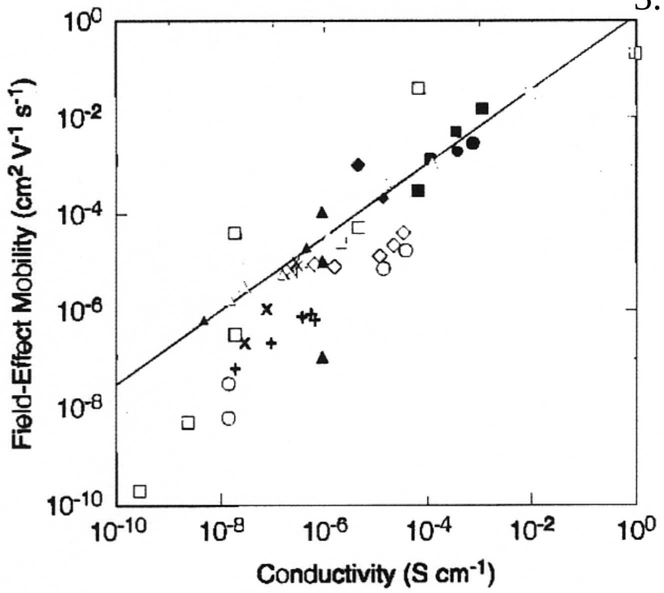
μ_{FET} : carrier mobility (cm^2/Vs)



PEDOT/PSS

50 ~ 80 cm^2/Vs

3.5 S/cm



H. E. Katz, Z. Bao, *J. Phys. Chem. B* **104** (2000) 671.

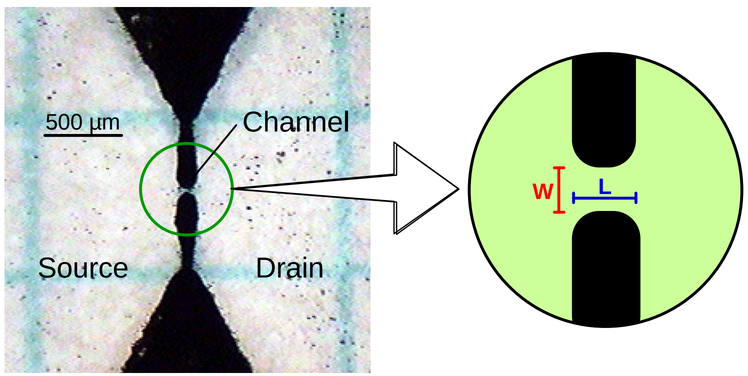
Optimization of FET

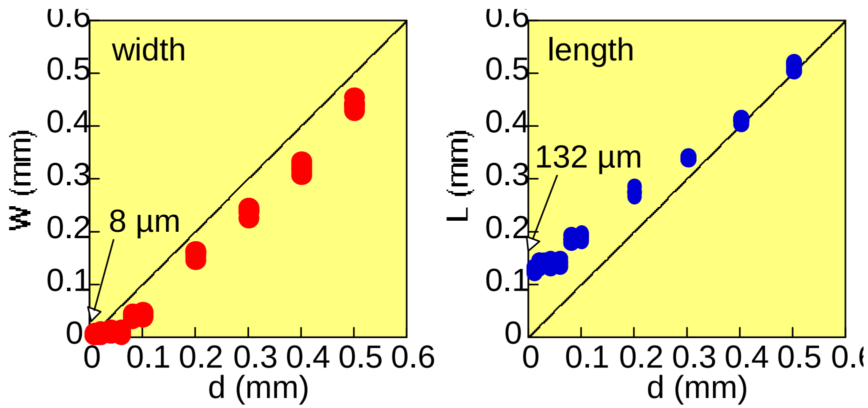
1. Substrate (flatness, smoothness etc.)

2. PEDOT/PSS solution (ethyleneglycol and DBS)

3. Insulator (material, thickness, unifirmity etc.)

4. Channel size (length, width, and thickness)





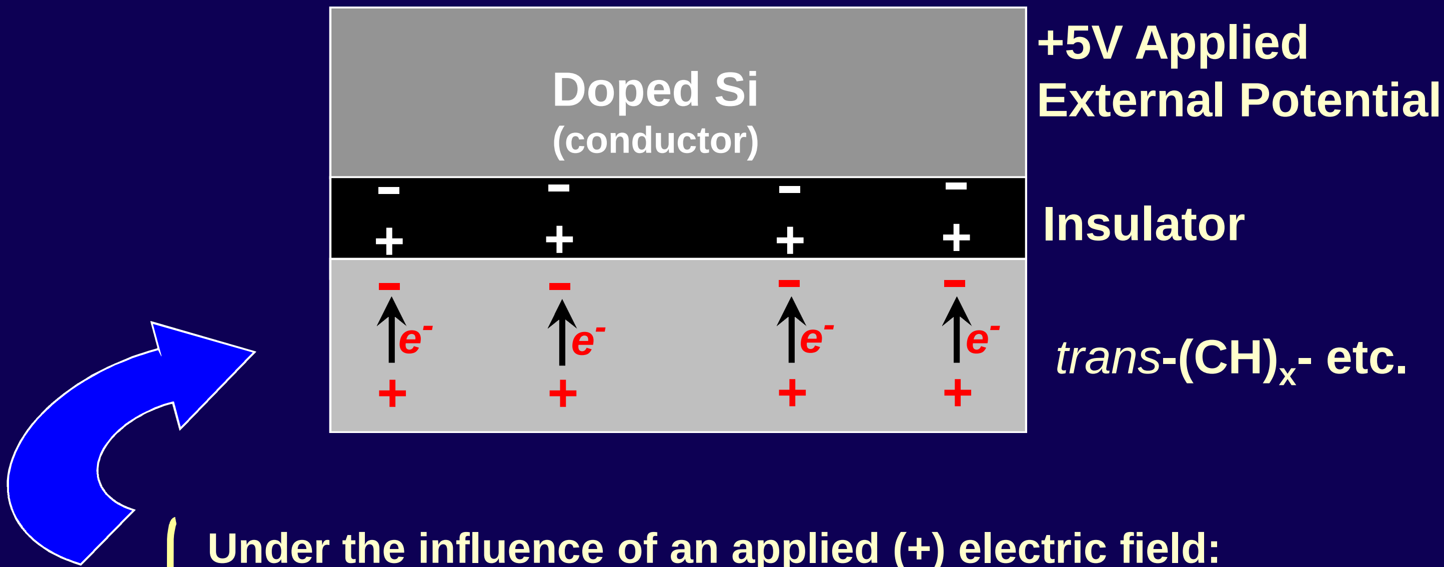
Conclusion

1. The ***line patterning***, a simple, easy, and inexpensive method for making conducting patterns, is applied to fabricate all-polymer FETs.

2. The FET, in which the conducting channel is already built, operates both in the depletion and enhancement modes under positive and negative gate voltages, respectively.

Charge Injection Doping*

(No dopant ions involved)



Under the influence of an applied (+) electric field:

Saw spectroscopic signature characteristic of solitons which disappear on removal of field. (Chemically reactive species might be formed)

Change in conductivity of ~2000 S/cm from +5V to -30V

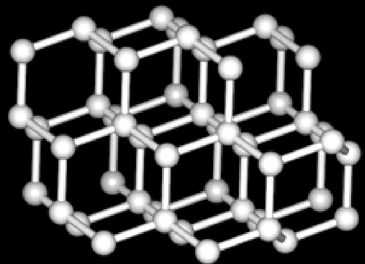
* R.H. Friend et al., Nature, **335**, 137 (1988); Phys Rev. Lett. **66,** 2231 (1991).
See also: C.T. Kuo et al., Synth. Metals **88**, 23 (1997): Synth. Metals **88**, 102 (1997).
See also: MacDiarmid, " The Polyanilines: A Novel Class of Conducting Polymers", in *Conjugated Polymers and Related Materials: The Interconnection and Electronic Structure,* Eds. W.R. Salaneck, I. Lundstrom, Oxford Scientific Press, UK., 1993, 73.

Capacitance Effects ?

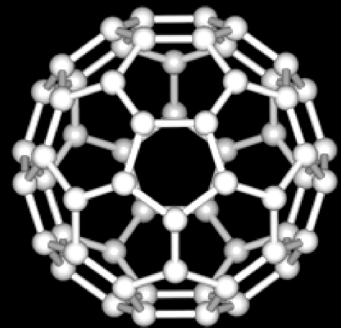
and/or

Faradaic *(electrochemical)* **effects?**

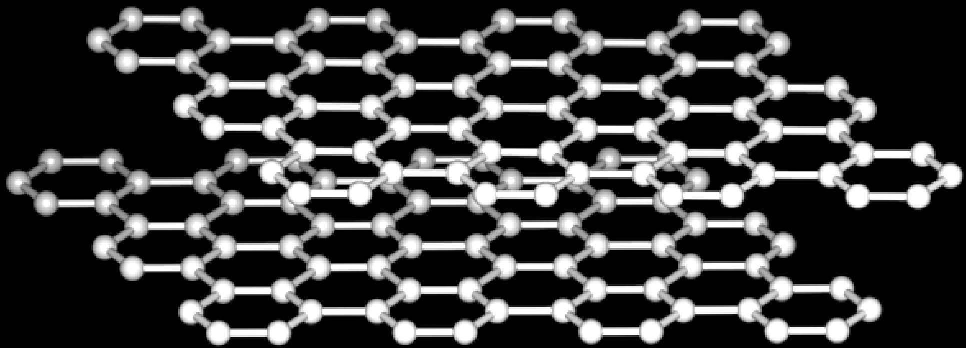
Forms of Carbon



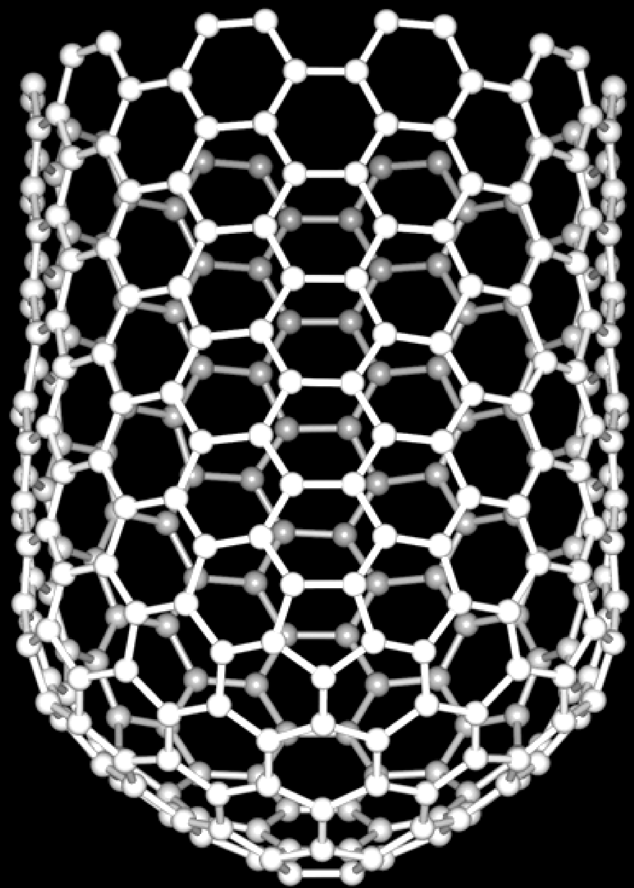
diamond



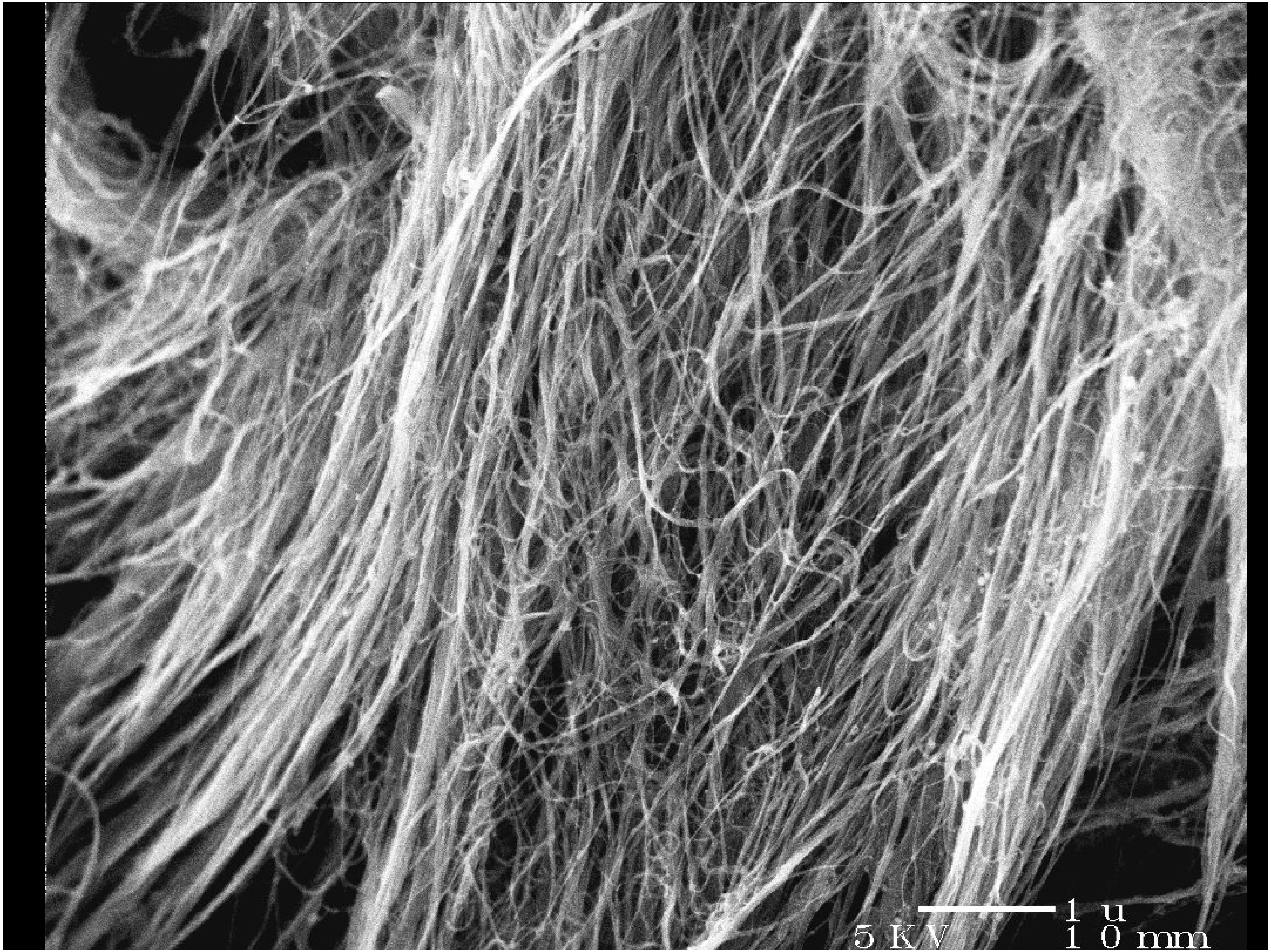
C_{60}
"buckminsterfullerene"

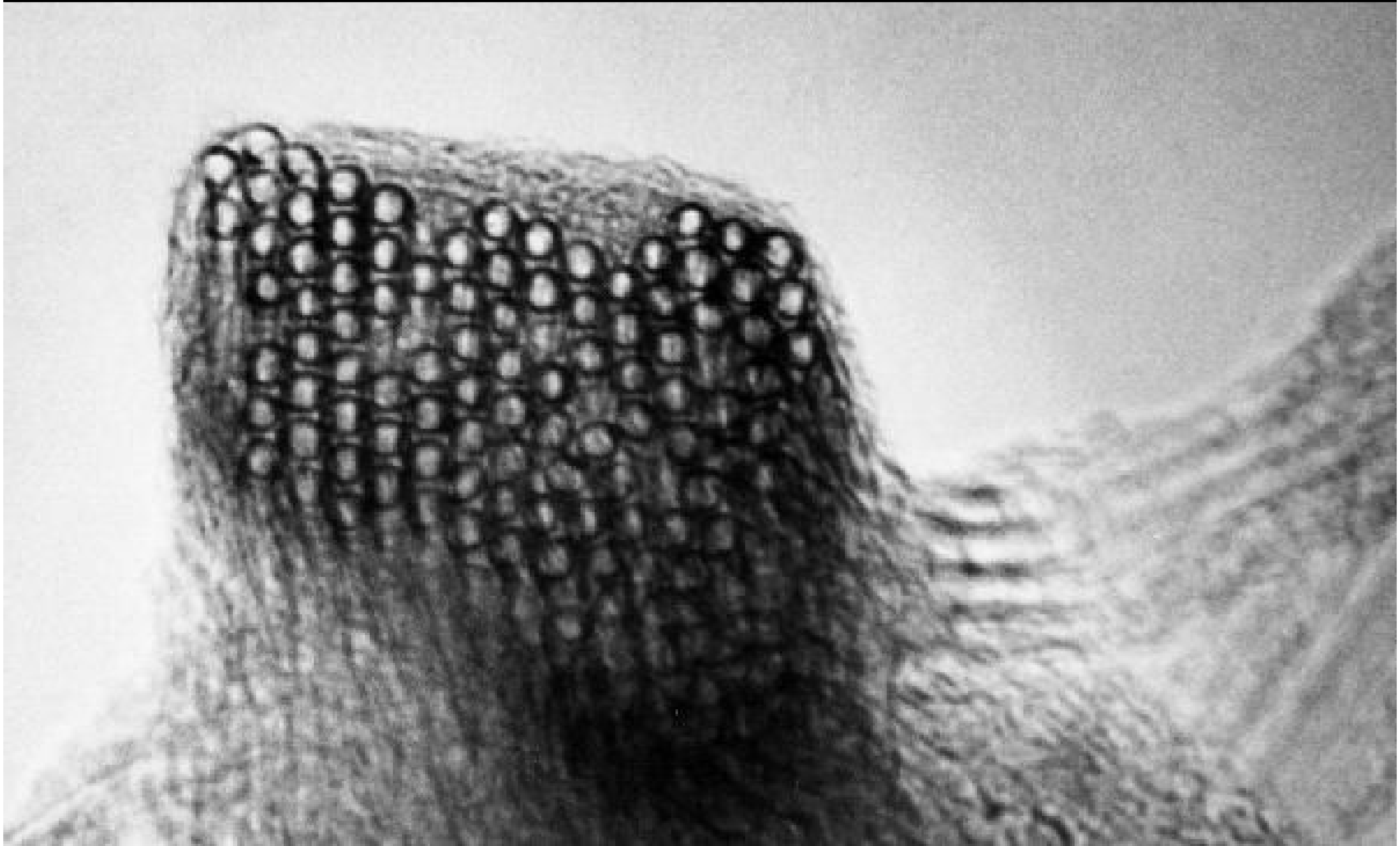


graphite

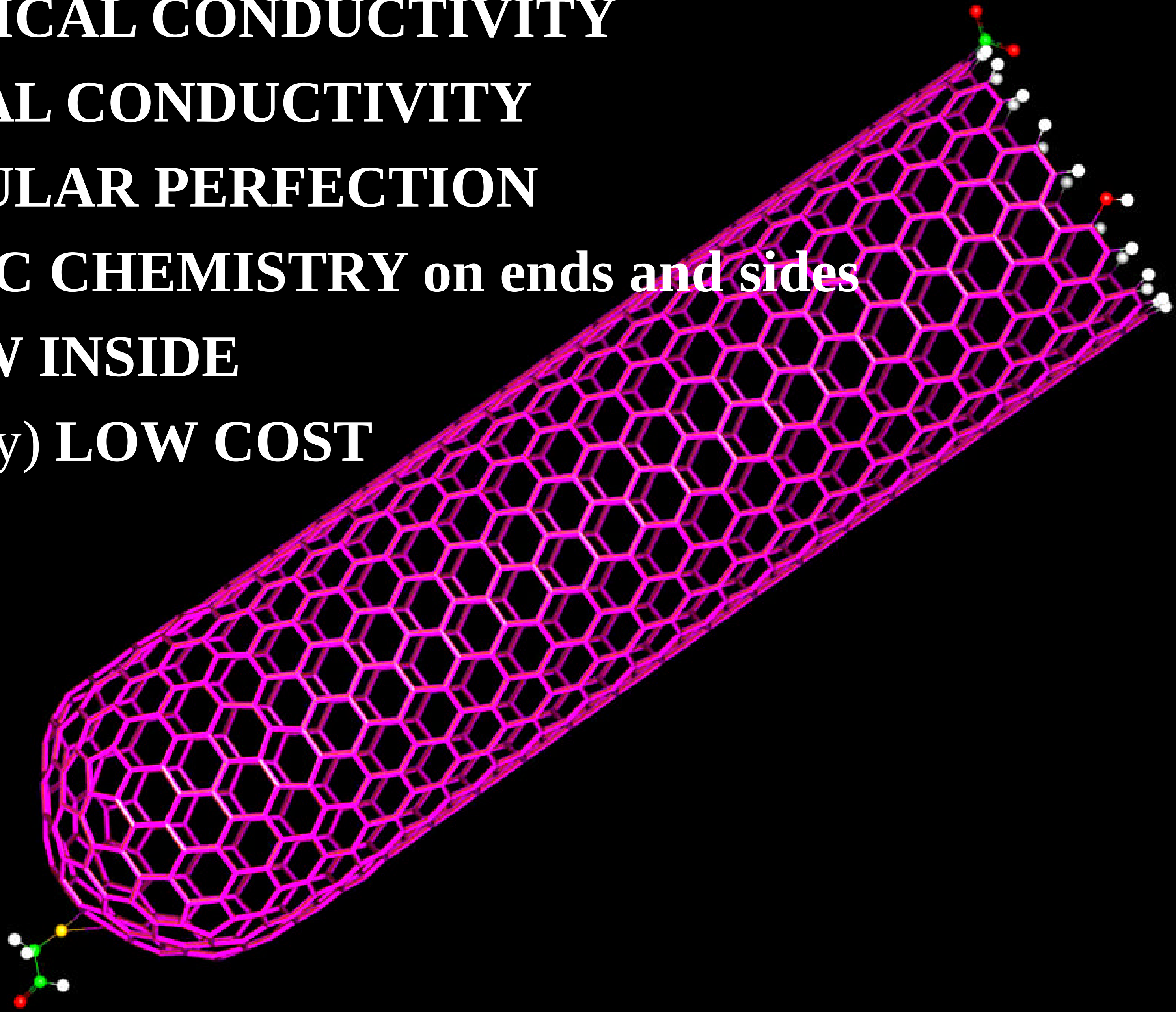


(10,10) tube

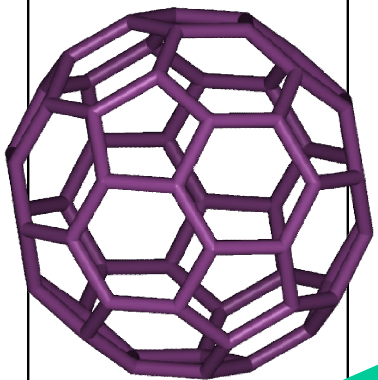

1 u
5 KV
1 0 mm

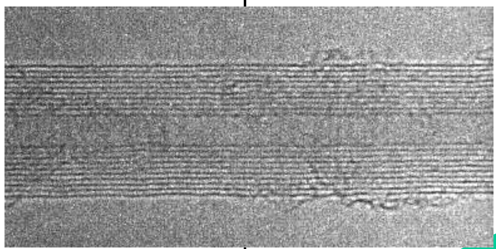


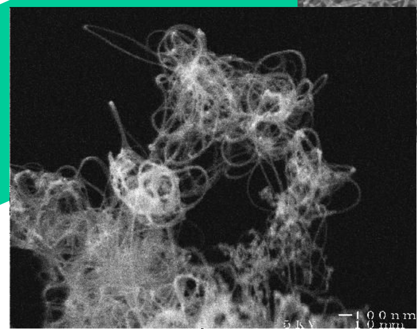
- **STRENGTH (~ 100 x STEEL, 10 x KEVLAR)**
- **ELECTRICAL CONDUCTIVITY**
- **THERMAL CONDUCTIVITY**
- **MOLECULAR PERFECTION**
- **ORGANIC CHEMISTRY on ends and sides**
- **HOLLOW INSIDE**
- (potentially) **LOW COST**

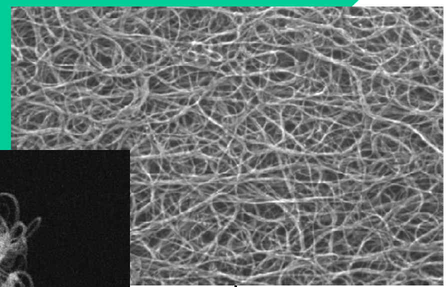


Fullerene Timeline









<u>1985</u>

Fullerenes discovered C_{60} and C_{70} (the smallest Buckytube) (Smalley)

<u>1990</u>

C_{60} visible quantities (Huffman, *et al.*)

<u>1991</u>

MWNT by carbon arc (Iijima)

<u>1993</u>

SWNT by carbon arc (Bethune, Iijima)

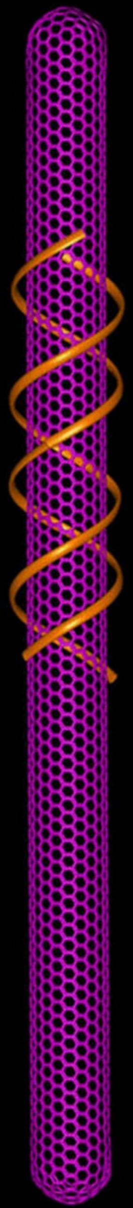
<u>1995</u>

SWNT research quantities by laser Oven method (Smalley)

<u>1998</u>

SWNT bulk quantities by HiPco process (Smalley)

Carbon Nanotechnologies Incorporated



Buckytube
with
DNA helix
shown for
scale

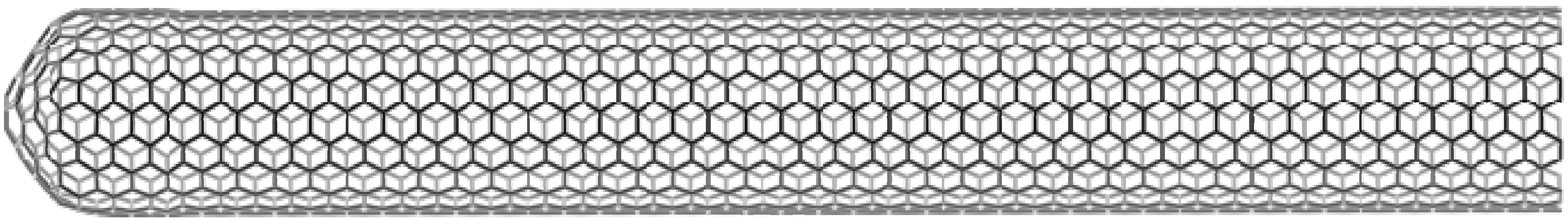
CNI

CNI Team

- **Dr. Richard Smalley**, 1996 Nobel Prize winner
- **Dr. Bob Gower**, former CEO of Lyondell Petrochemical
- **Drs. Ken Smith** and **Daniel Colbert**, Rice faculty members, now full-time with CNI
- **Gordon Cain** and **Bill McMinn,** Investors (and collaborators)
- **20 Employees** – Engineering, Research, Marketing
- **Kellogg / Brown & Root,** Engineering services and Pilot Plant space

CNI's Mission:

To Enable the Development of
Materials and Electronics Based on
Single-Wall Carbon Nanotubes



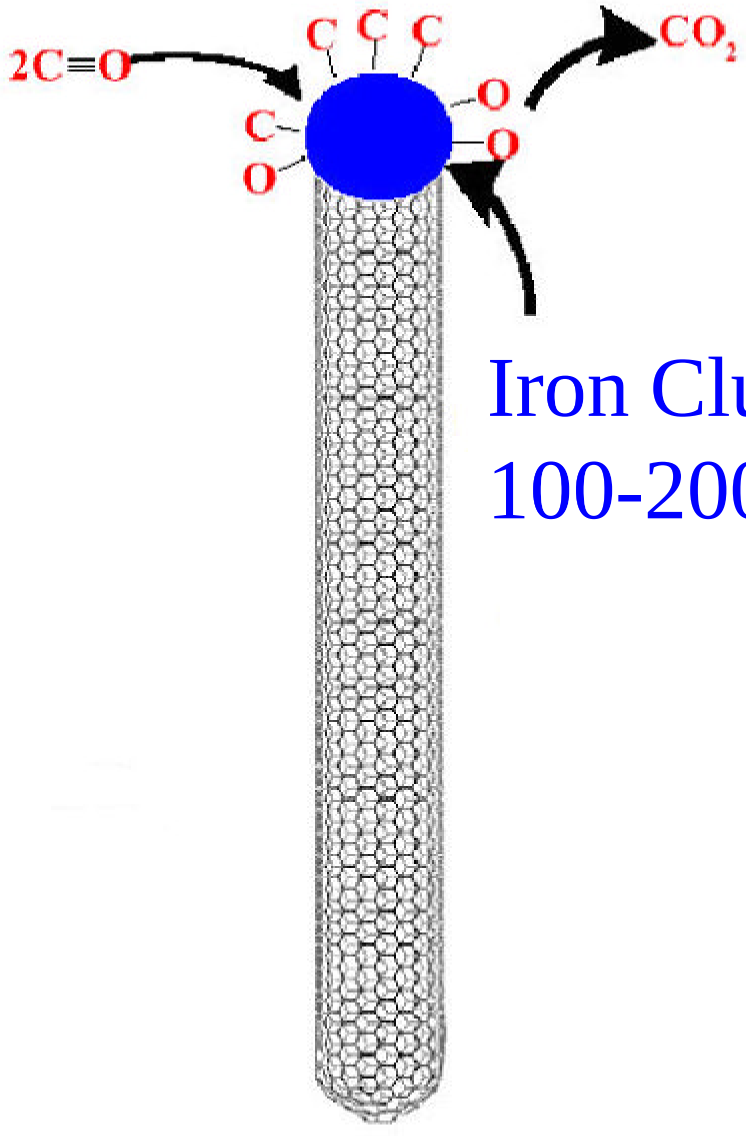
CNI's Strategy:

- Implement commercial-scale SWNT production
- Develop and exploit new SWNT markets

CNI's HiPco Process

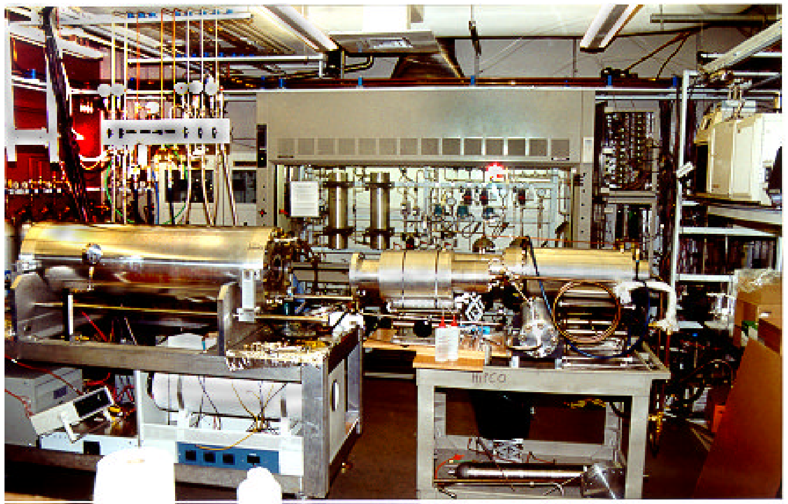
- Single-step, gas-phase process for production of single-wall carbon nanotubes (SWNT)
- Common industrial feedstock (CO) readily available
- Inexpensive catalyst
- Product is predominantly pure nanotubes and catalyst residue
- Catalyst residue is easily removed when necessary, and will decrease as process is developed further

30-100 atm. CO
~1000 ºC
+
$Fe(CO)_5$
Precursor



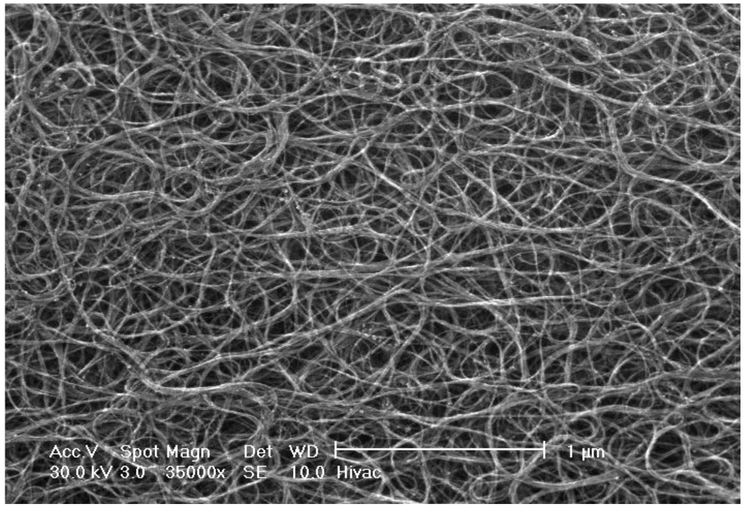
Iron Cluster
100-2000 atoms

HiPco



1 step

Gas phase



CNI believes this is the only process that can now be commercialized to produce SWNT economically

CNI Timeline

1998	2000	2001	2002	2003-2004
HiPco Process	CNI founded	CNI licenses Rice IP	Pilot Plant	
		SWNT samples for testing	Larger quantities for market development	Full-scale Plant

CNI Intellectual Property

- Patents in all known methods for SWNT Production
- Compositions of matter
  - Ropes, arrays, composites, and others
- Enabling technology
  - End, sidewall, and non-covalent derivatization
- End-use applications
  - Composites, fiber, electronic, chemical process, fillers for polymers, solar energy, batteries, fuel cells, etc.

Production Development

- Research at Rice University
  - Tubes@Rice: 1 g/day (purified)
  - Mark I NASA prototype: 5-10 g/day
  - Mark II (Sept. 2000): 20-50 g/day

- Pilot Plants (2001-2002): 0.1-2 lbs/day

- Initial Commercial Plant (2003-2004): 0.5 – 1 ton/day

PRIMARY MARKET AREAS

ELECTRONIC

Conductive Plastics
- Electrostatic Dissipation
- Shielding
- Stealth

Energy Storage
- Battery
- Supercapacitors
- Fuel cell
- Solar cells

Electronic Materials & Devices
- Conductive inks, pastes, and adhesives
- Electronic mounting and packaging
- Device and microcircuit components
- Optoelectronics materials
- Lightning arrestors
- Transmission lines and wires

Field Emission
- Phosphor excitation (FPD and lighting)
- Electron device cathodes

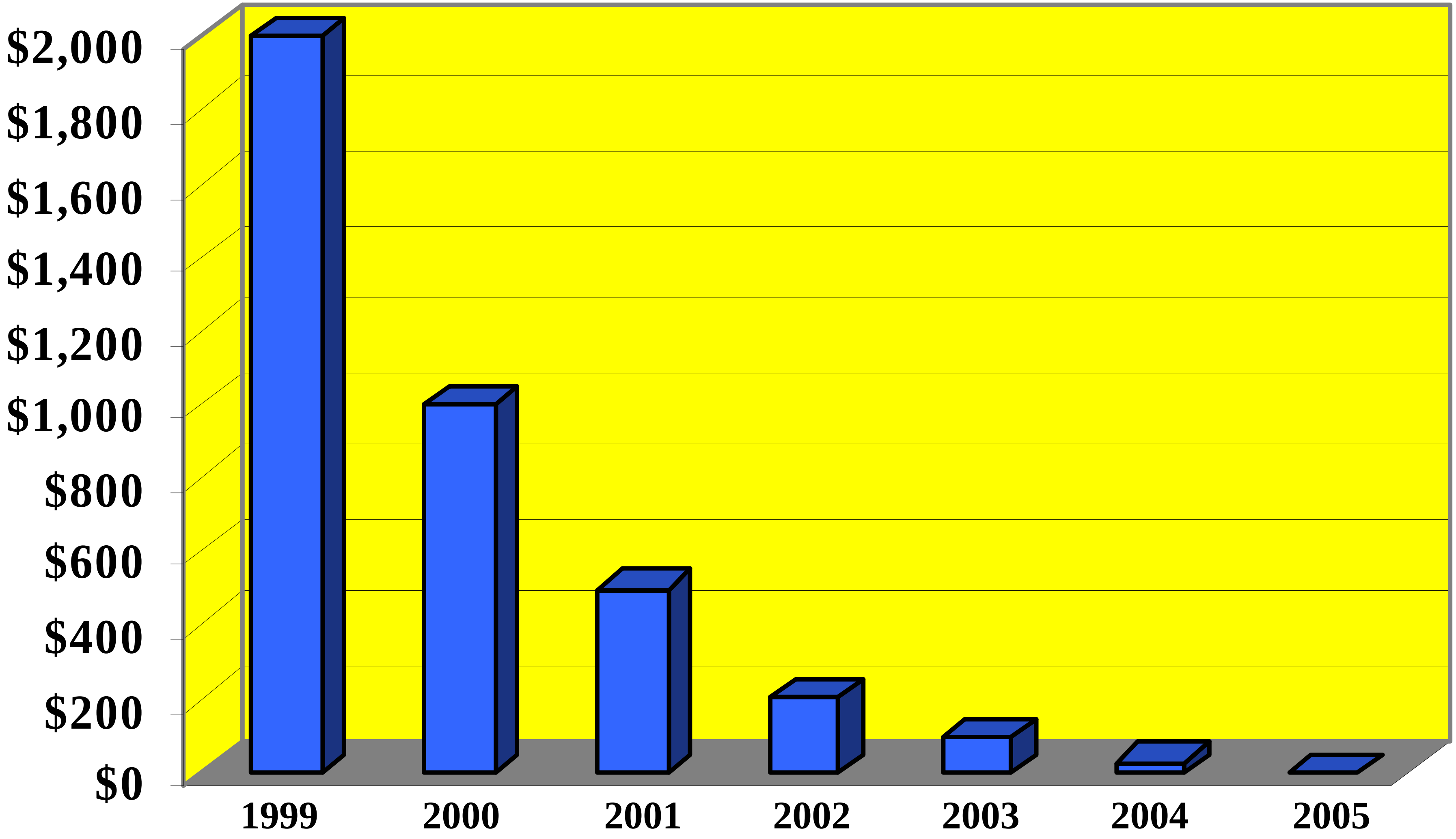
Miscellaneous
- Actuators and transducers
- Lightning protection
- Sensors

THERMAL
- Thermally conductive paints, pastes, coatings
- Thermally conductive fibers
- Thermally conductive cables, wires, and tubing

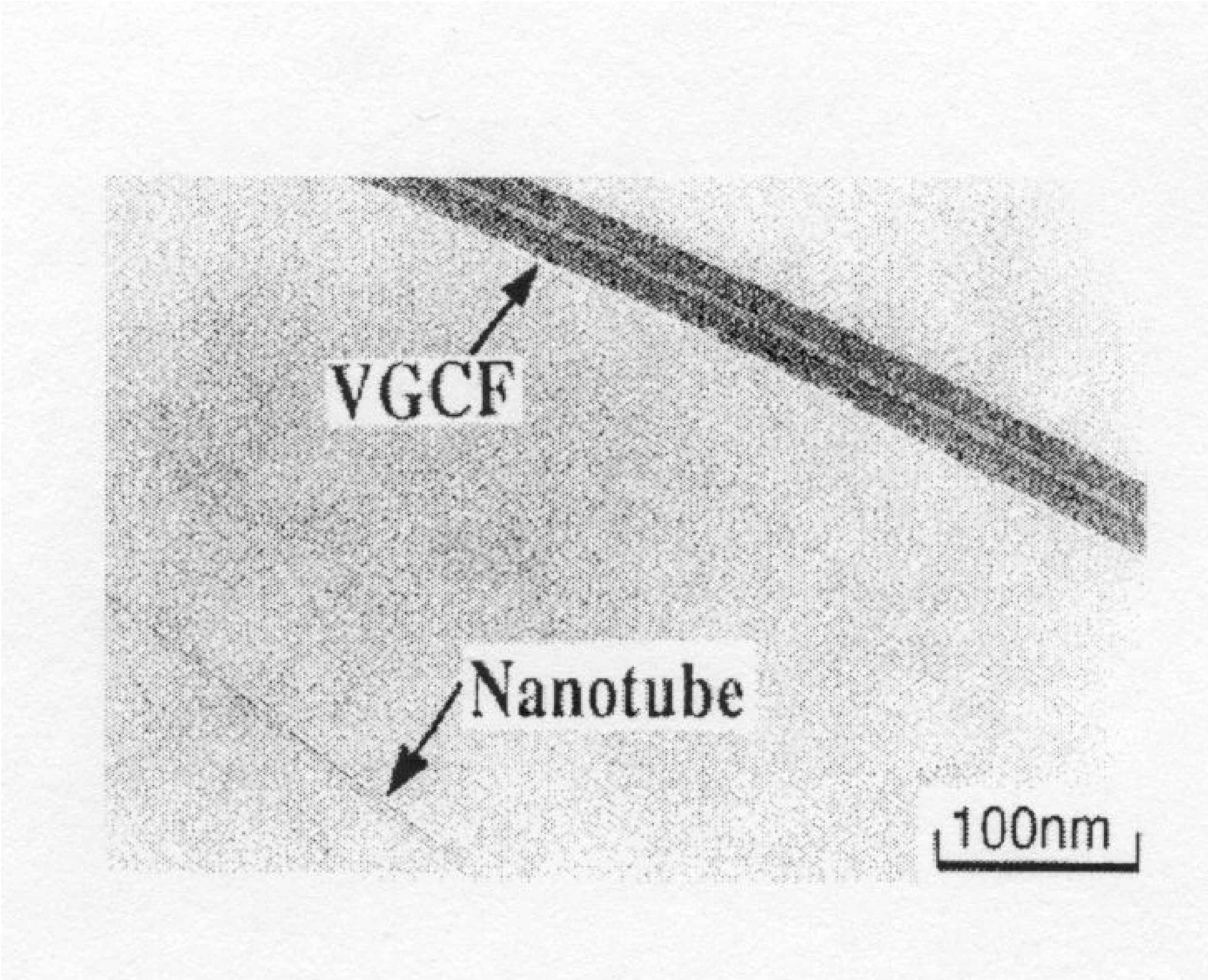
MECHANICAL
- High-strength composites
- Films and sheets
- Coatings – wear-resistant and low-friction
- High strength fiber – pure and composite

CHEMICAL/OTHER
- Filters, separators, adsorbants
- Catalyst supports
- Biomedical coatings, objects
- Hydrogen storage
- Anti-fouling, anti-corrosion, and anti-bio coatings

SWNT Pricing Per Gram



CNI CONFIDENTIAL

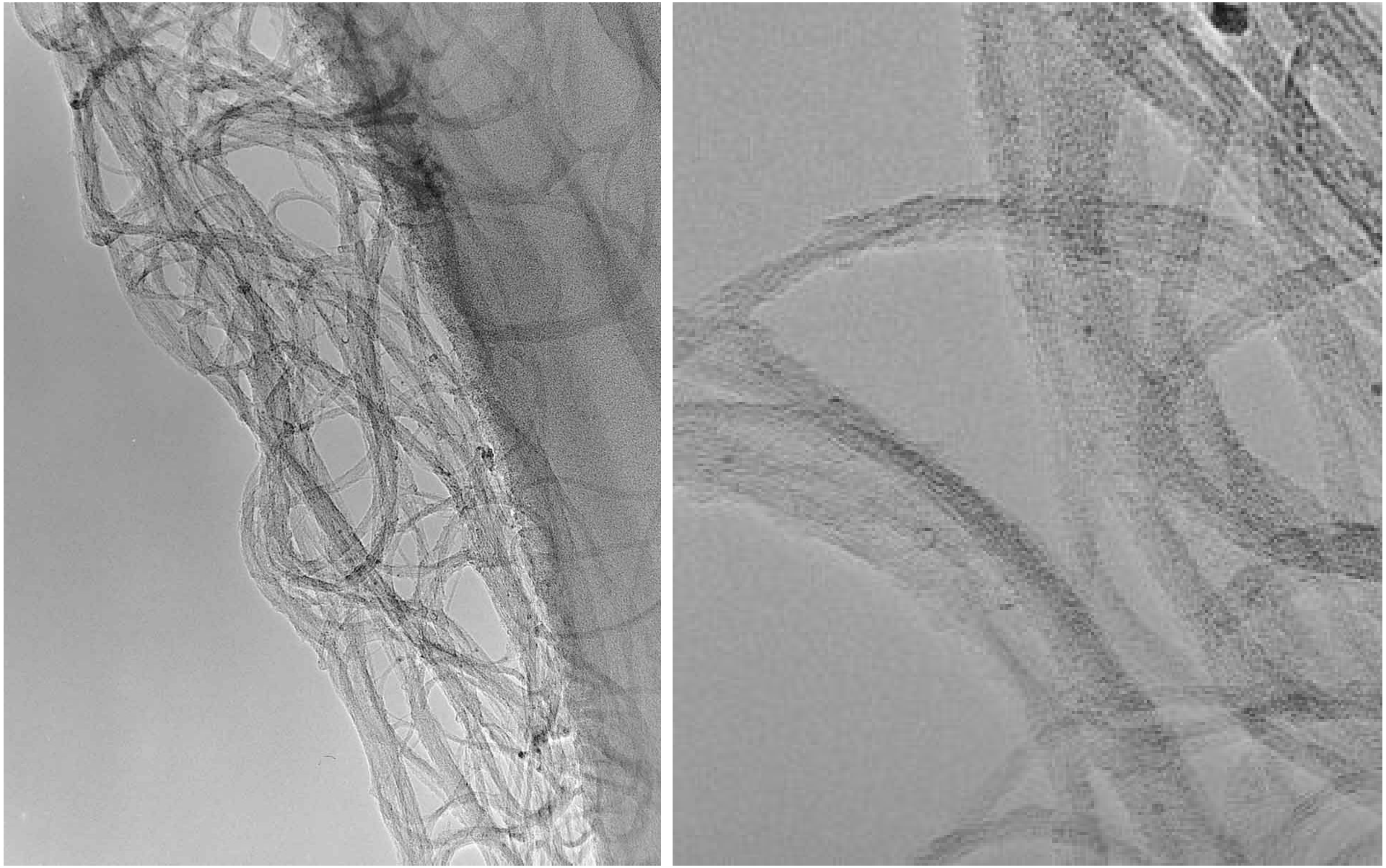

VGCF
Nanotube
100nm

SWNT

- Made by all gas-phase HiPco process
- Diameter of 0.7-1.5 nm
- ***Molecularly perfect***
- Stronger, tougher, stiffer
- Superior electrical conductivity
- Superior thermal conductivity
- Self-assemble into extended networks
- Developing production technology

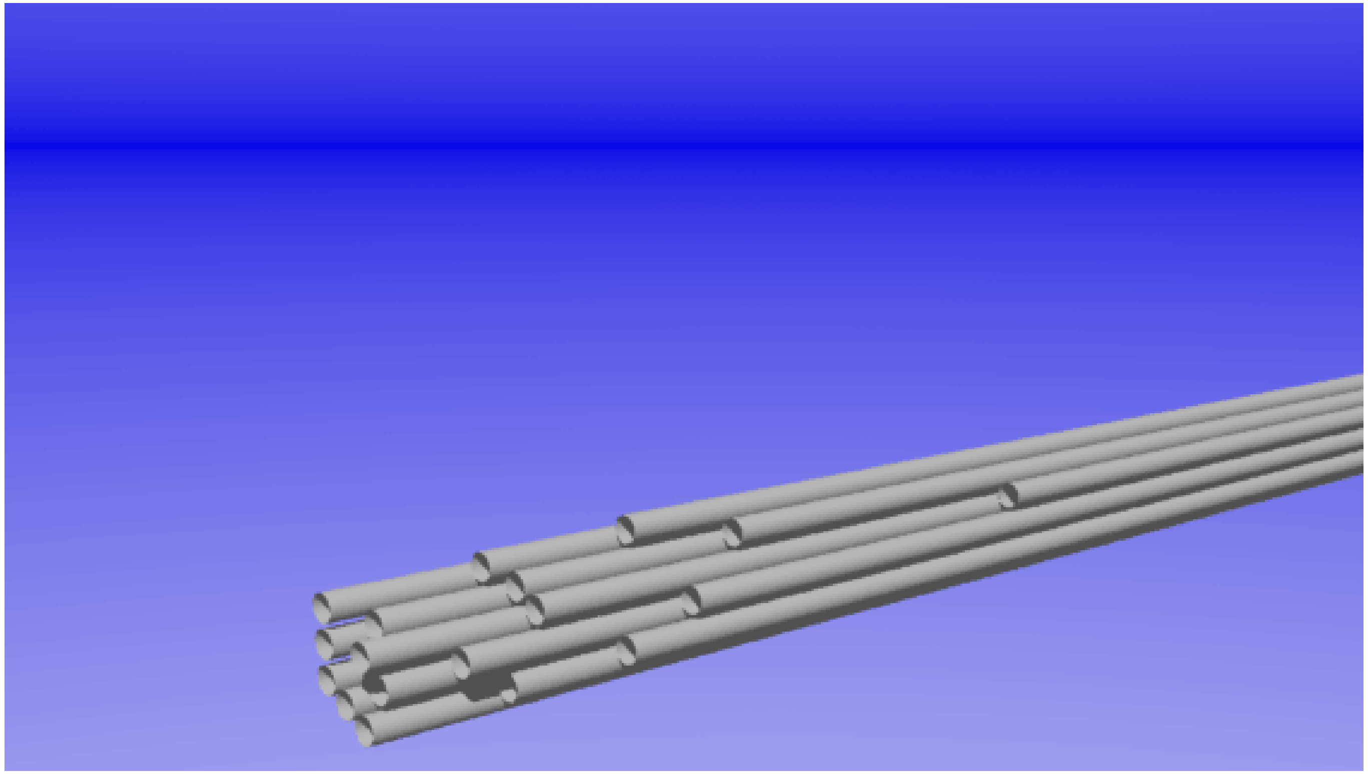
Carbon Nano-Fibers

- Made on solid catalyst supports
- Diameter 20-200nm
- Frequent defects
- Mechanically inferior
- Lower electrical conductivity
- Lower thermal conductivity
- Do not self-assemble
- Mature production technology



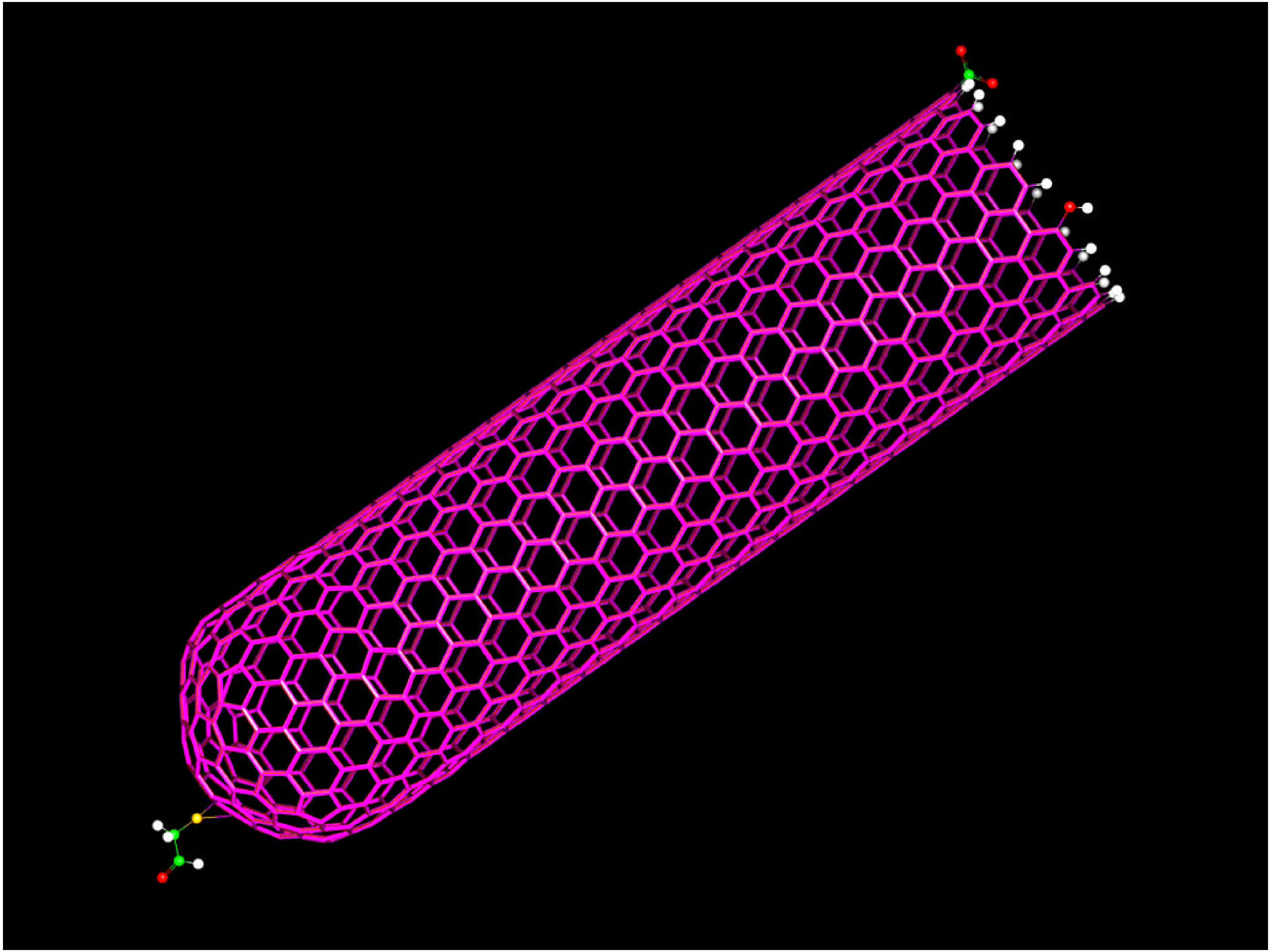
HiPco Nanotubes

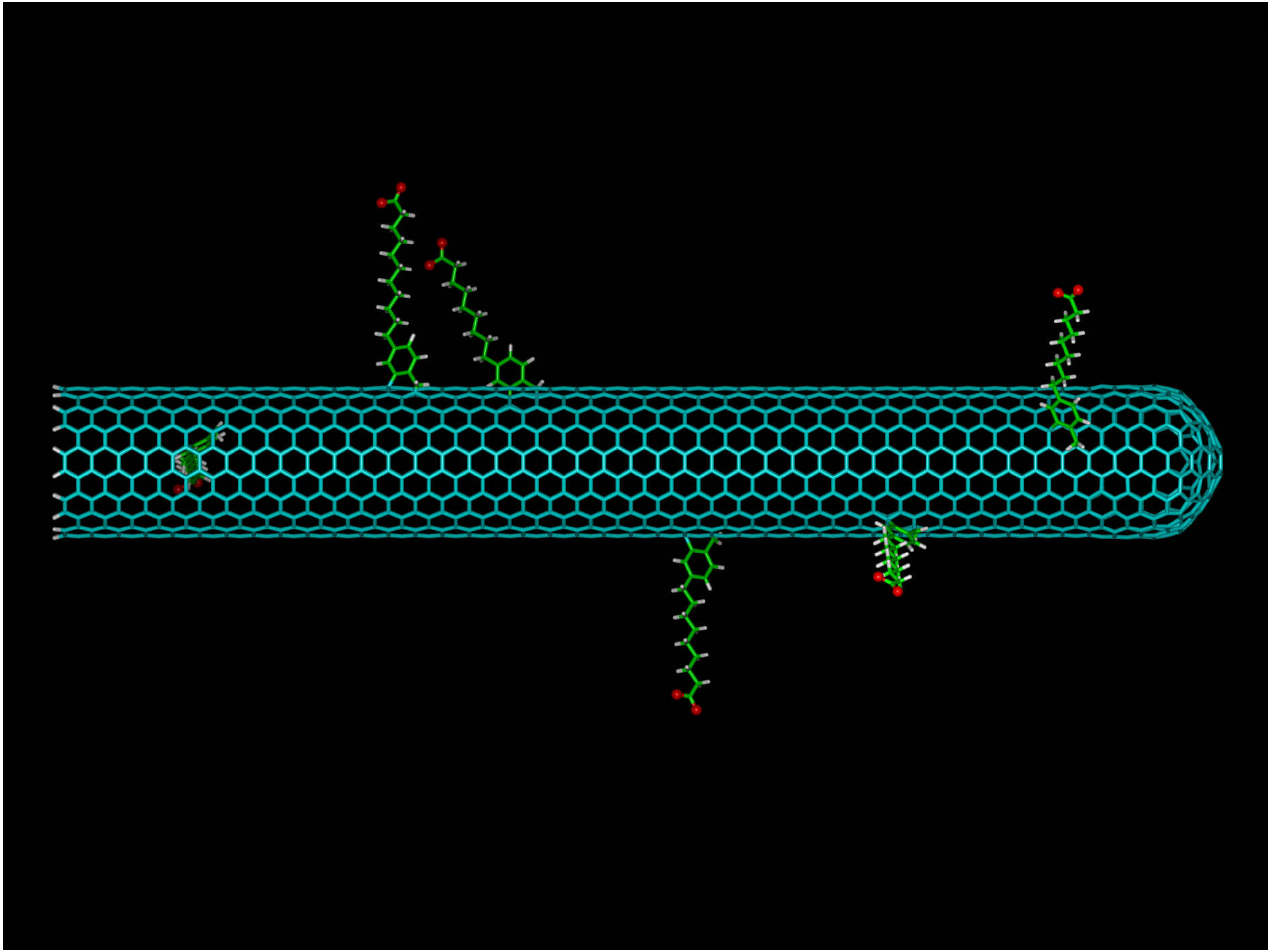
Roping of Carbon Nanotubes

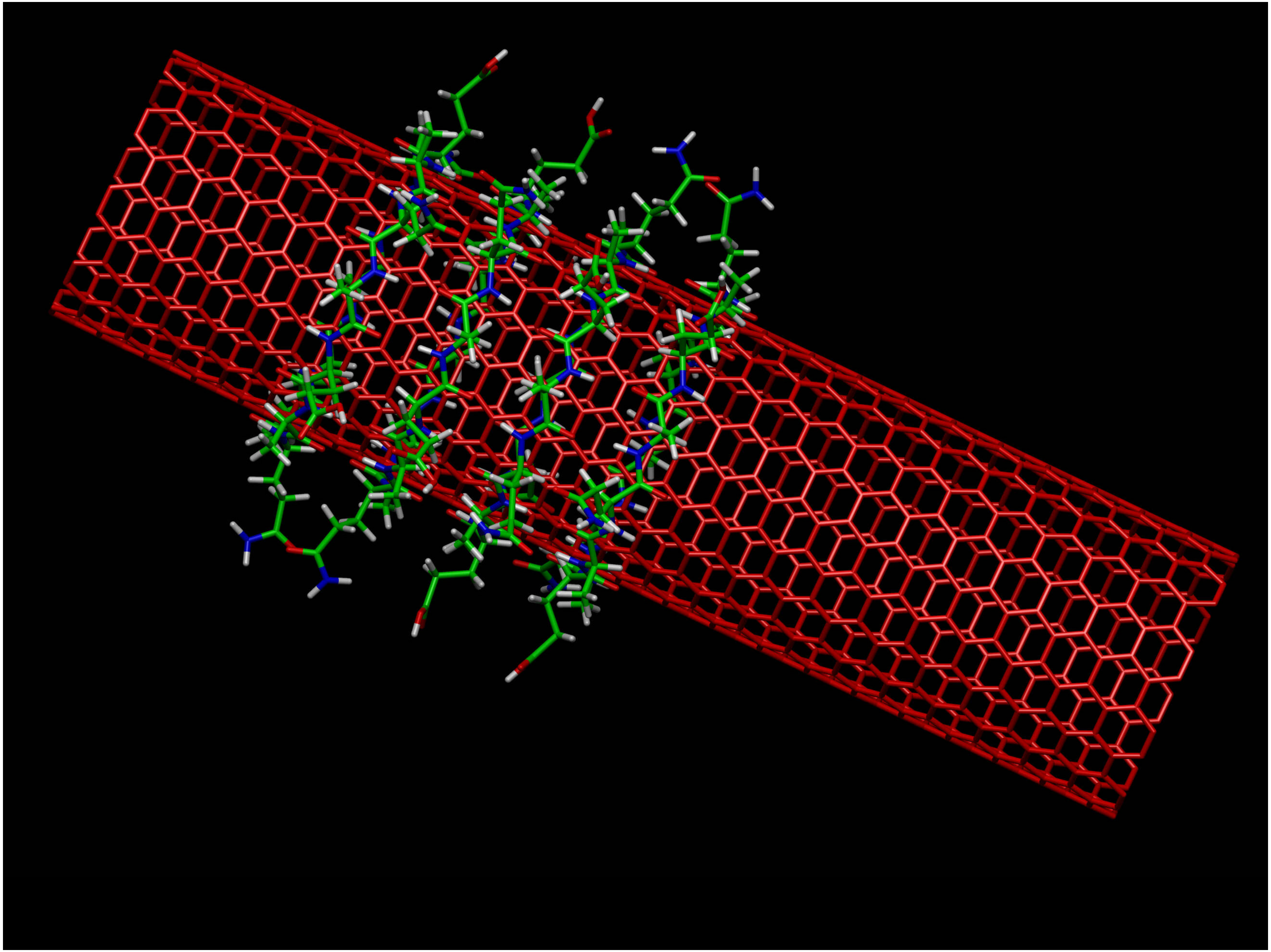


SWNT Additives to Polymers

- Main research has been in producing anti-static and EMI-suppressing compounds – conductivities achieved range between 0.001 and 1 Siemens/cm
- Higher SWNT loadings in some conducive composites show some increase in tensile modulus (~30%) and strain-to-failure (~100%)
- Further development of SWNT – polymer nano-composites depends on :
  - Understanding dispersion techniques
  - Focus on specific property for enhancement in composite (electrical, thermal, mechanical, etc.)
  - Utilization of unique aspects of SWNT (roping, derivatizability, strength, thermal and electrical conductivity, etc.)

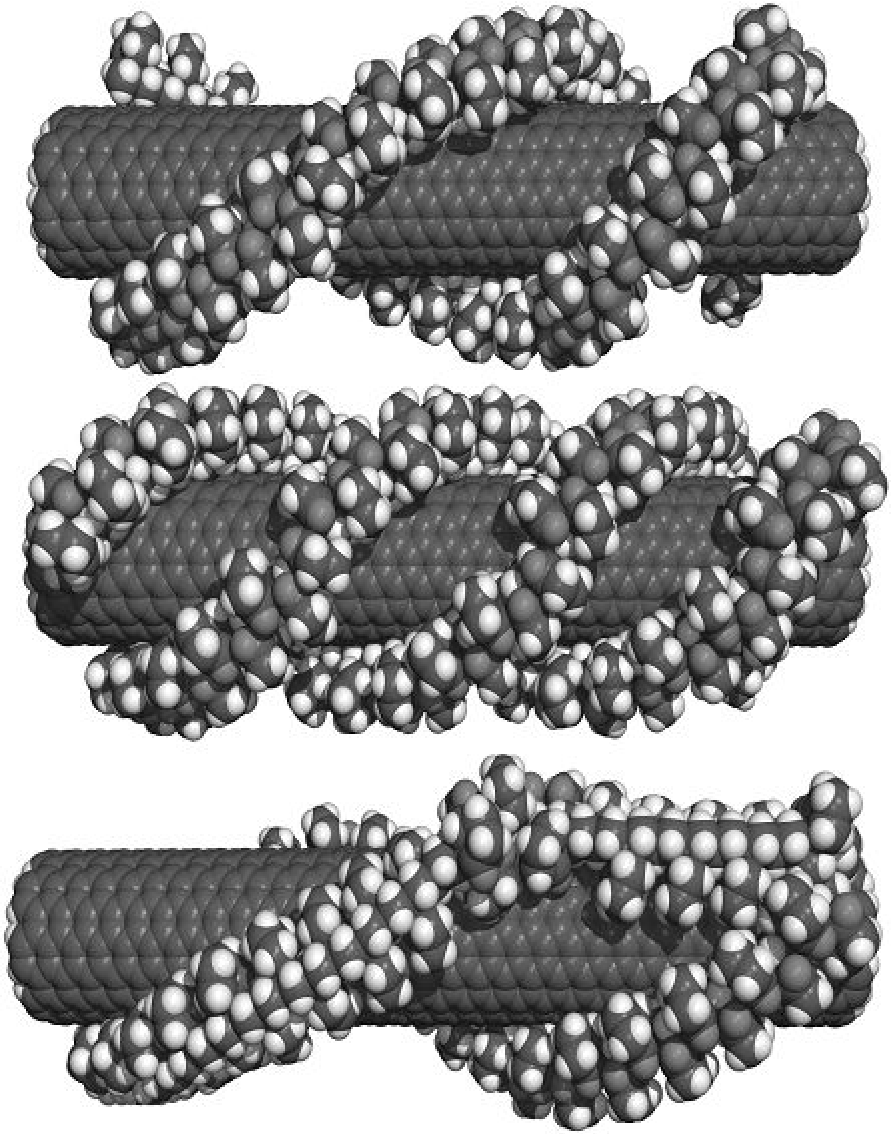






Tubes & Polymers

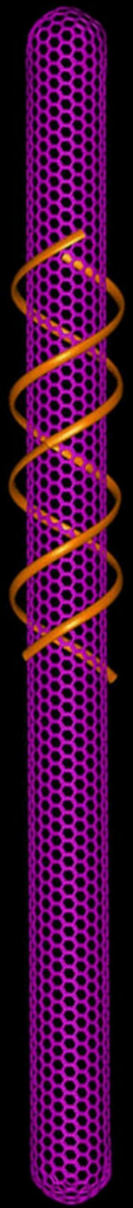
- Enhances suspension
- Interacts with matrices
- Retains electrical properties
- Enables new composites
- Enables control of roping and network formation



8,8 SWNT wrapped with PVP

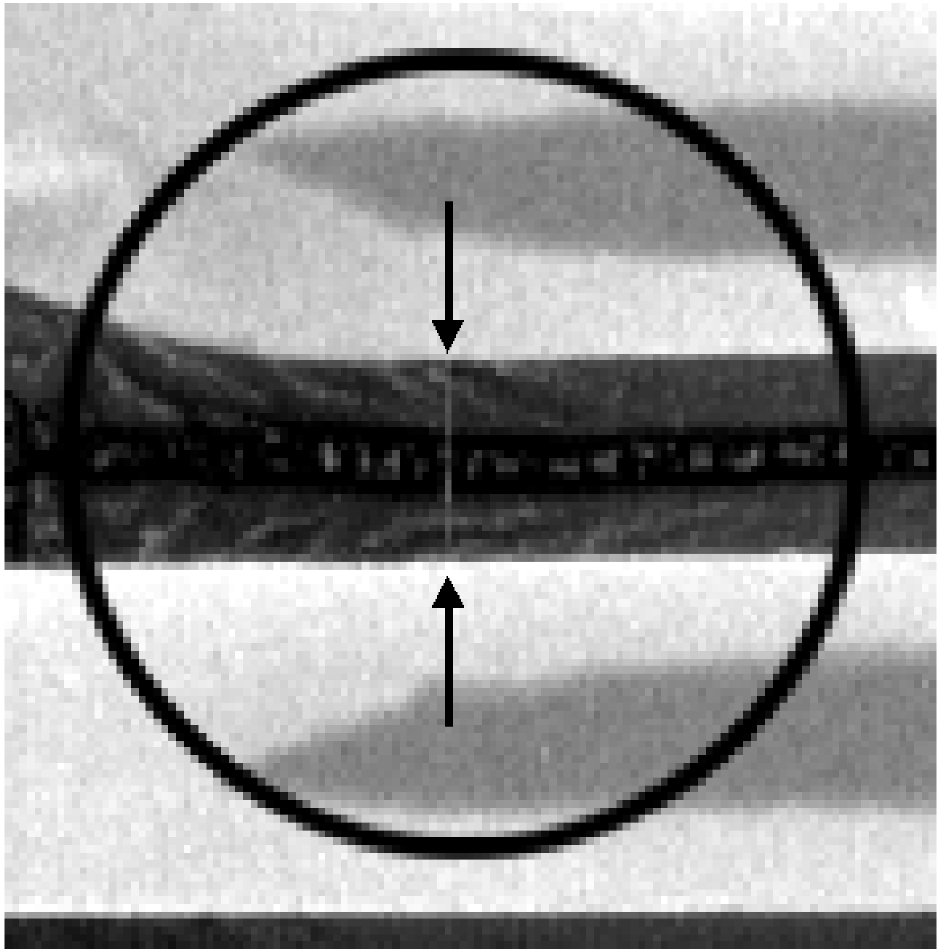
Carbon Nanotechnologies Incorporated

CNI



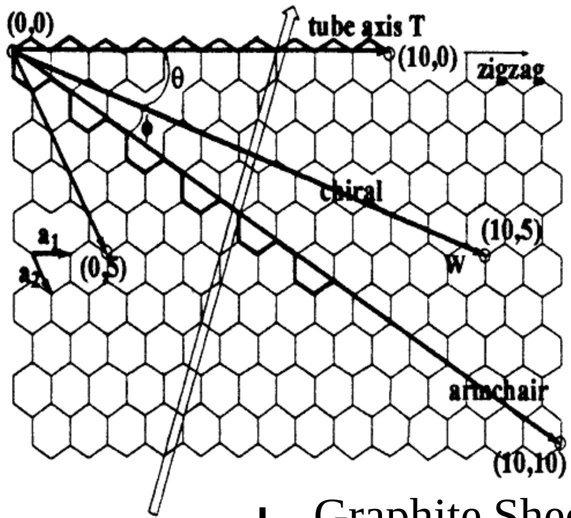
Buckytube
with
DNA helix
shown for
scale

Nanotechnology Uses Structures Smaller than 0.1 Micron (or about 1/500 of the diameter of a human hair)

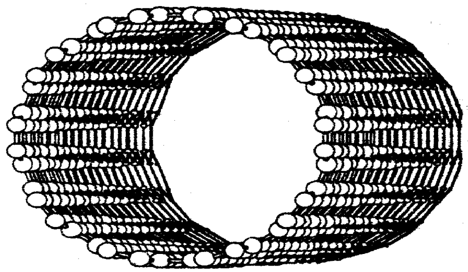


2 microns
(25 times
diameter
of your hair)

World's smallest artificial muscle!



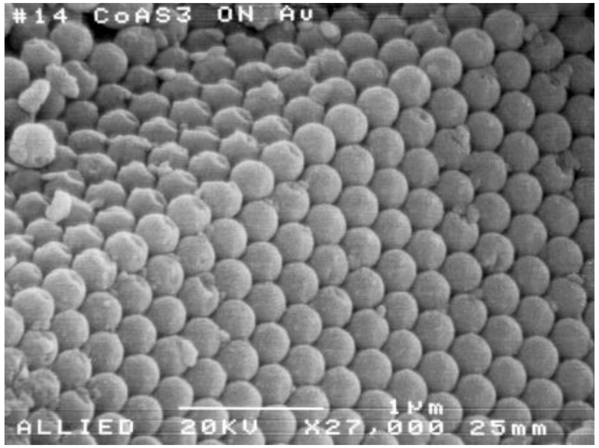
Graphite Sheet



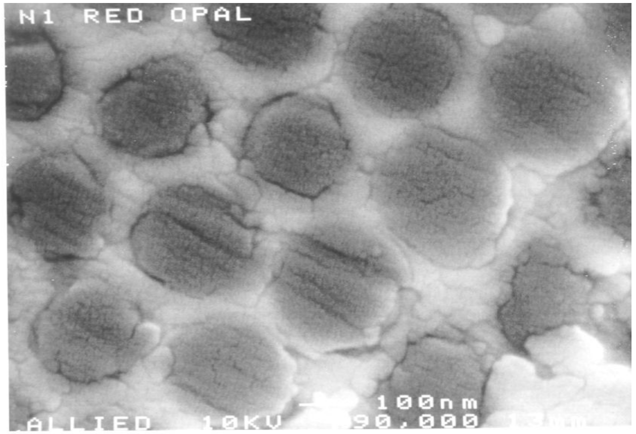
Carbon Nanotube
(1/50,000 of diameter of your hair)

THE FABRICABILITY GAP MUST BE BRIDGED –
Between the micron scale of lithography and the atomic scale

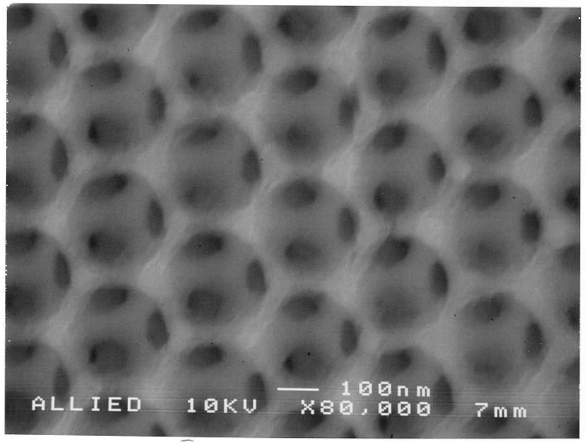
We developed technology to do this, thereby making photonic crystals



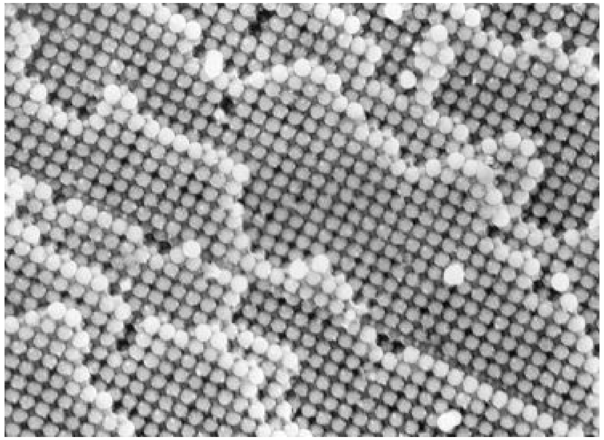
Self-assemble spheres



Infiltrate sphere arrays



Extract original spheres, leaving inverse replica



Infiltrate inverse replica & Extract, leaving sphere array

We have used our method to make new magnetic, superconducting, and optical materials.

All are photonic crystals, the optical analogue of semiconductors.

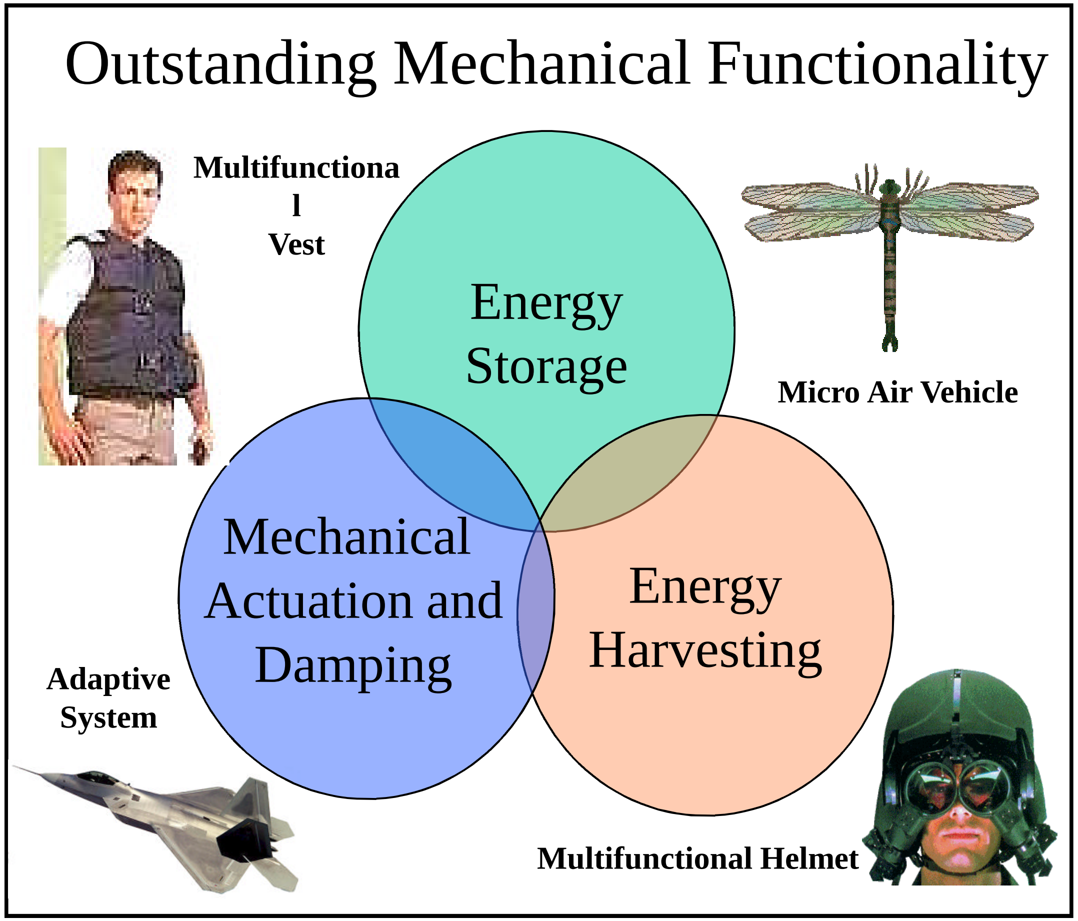
Exciting results are a laser that lases in 3D, switchable optical circuit elements for multiplexing, and a candidate infrared camouflage material.

Funded at UTD through Army MURI program.

MULTIFUNCTIONAL CARBON NANOTUBE FIBER COMPOSITES

$2.7 Million from DARPA to UTD as prime contractor anticipated

PI: Ray Baughman



GOAL:

Demonstrate feasibility of carbon nanotube composites combining mechanical functionality with

(a) mechanical actuation,

(b) energy storage,

(c) mechanical dampening,

(d) energy harvesting,

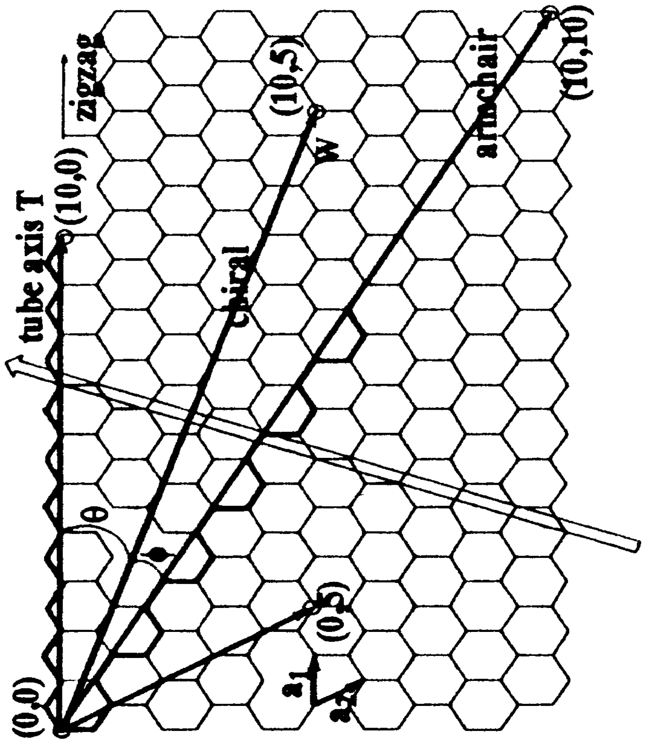
(e) sensing, and/or

(f) camouflage functionalities.

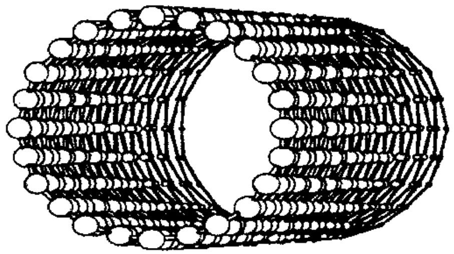
New Actuator Material:
Single-Wall Carbon Nanotubes

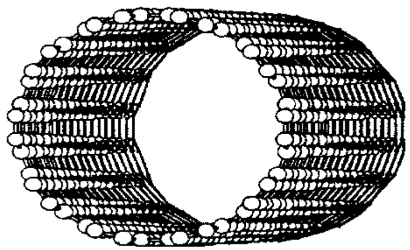
Modulus: 6 million kg/cm^2 Strength: 0.3 million kg/cm^2

Surface Area: 1500 m^2/gm Conductivity: 5000 S/cm



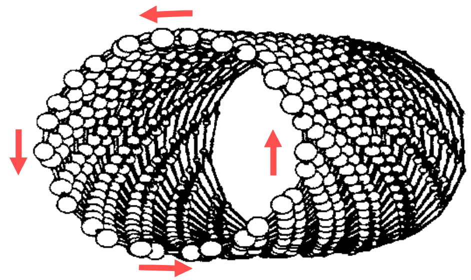
(12, 0)
Zigzag



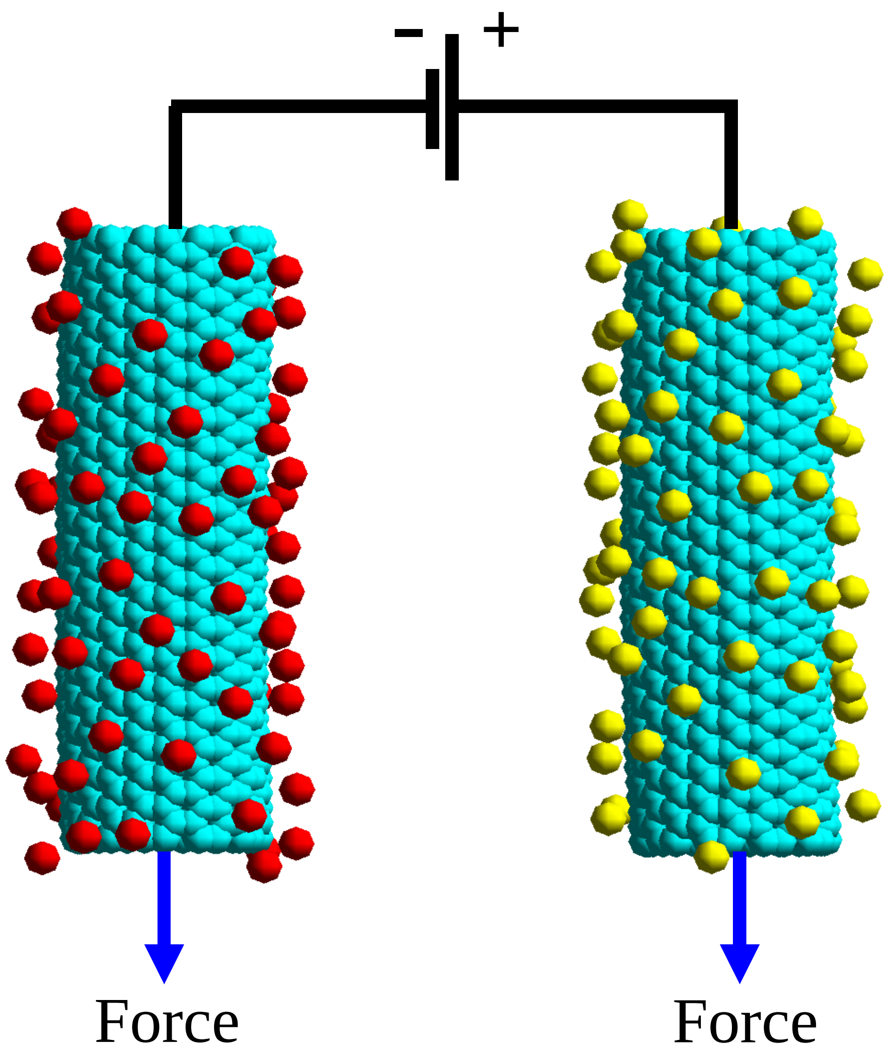


(10, 10)
Armchair

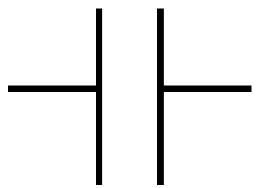
(10, 5)
Chiral



Double Layer Charge Injection Is Important for Energy Storage, Energy Harvesting, Mechanical Damping, Actuation, and Other Functionalities



Ferroelectric actuators are ordinary capacitors.



Our new actuators are super capacitors: The effective separation between plates is in a nm.

WORK/CYCLE COMPARISON SHOWS WHY DARPA INVESTS IN OUR NANOTUBE ACTUATORS

Material	Y(GPa)	ε_m	$Y\varepsilon_m^2/2$ (J/cm^3)	$Y\varepsilon_m^2/2\rho$ (J/kg)
Piezoceramic	64	0.1 %	0.32	4.25
Magnetostrictor	100	0.2 %	0.2	21.6
PZN-PT Single Crystal	7.7	1.7 %	1.0	131
Polyurethane Elastomer	0.02	4 %	0.016	13
P(VDF-TrFE) Electrostrictor	0.38	4 %	0.3	160
Non-bundled SWNT (theory)	640	1% (1 V)	29	24000.

29x by volume

150x by weight

OUR NANOTUBE ACTUATORS ALREADY GENERATE 100 TIMES THE FORCE OF NATURAL MUSCLE

LARGE ACTUATORS

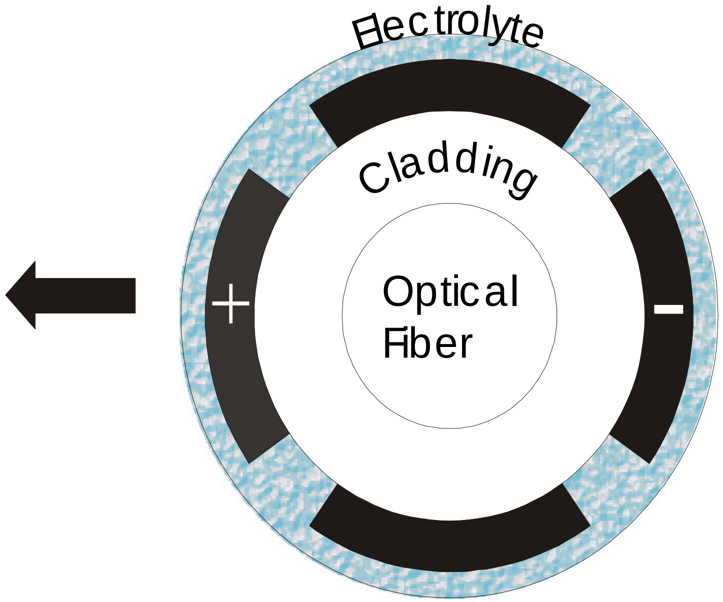
POTENTIAL

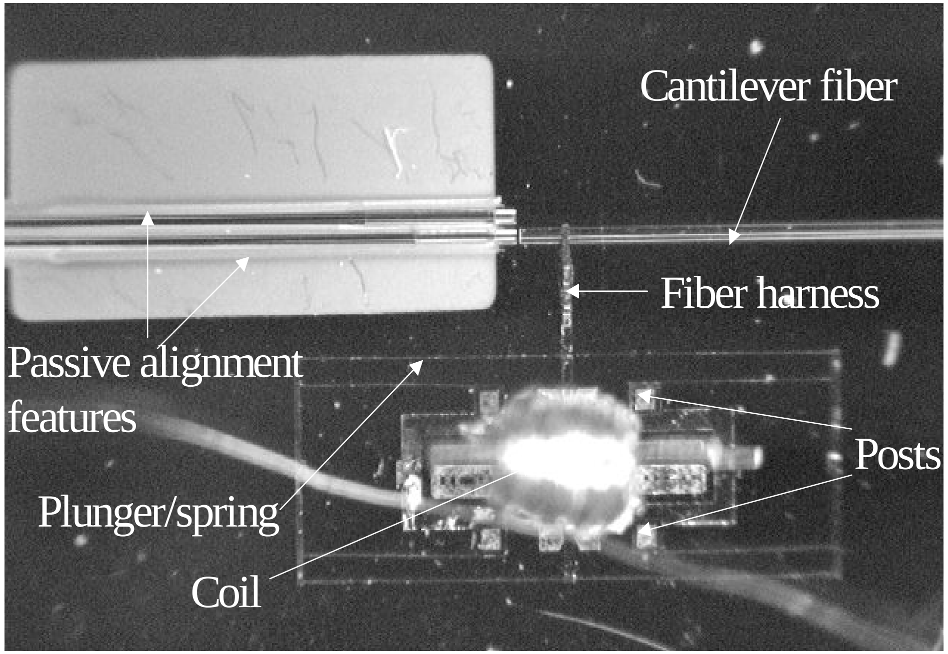
- Gravimetric work capabilities ten times ferroelectrics.
- Stress generation capabilities ten times ferroelectrics.
- Cycle life should be large.
- Large stroke (above 1%).
- Ten times lower needed voltage than ferroelectrics.
- Operation to above 1000^{o} C.

SOME POSSIBILITIES

- Actuation for hostile environments (temperature or radiation): aircraft engines, down hole, planetary exploration
- Man-like robotics (prosthetics, body assists, artificial heart)

MICROACTUATORS: OPTICAL FIBER SWITCH



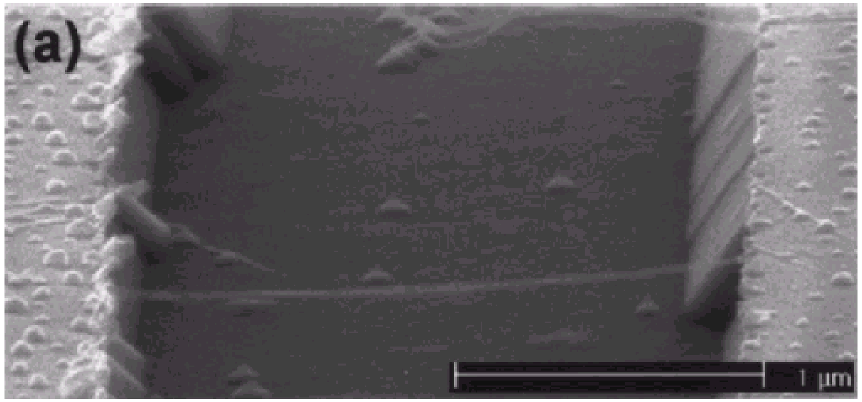


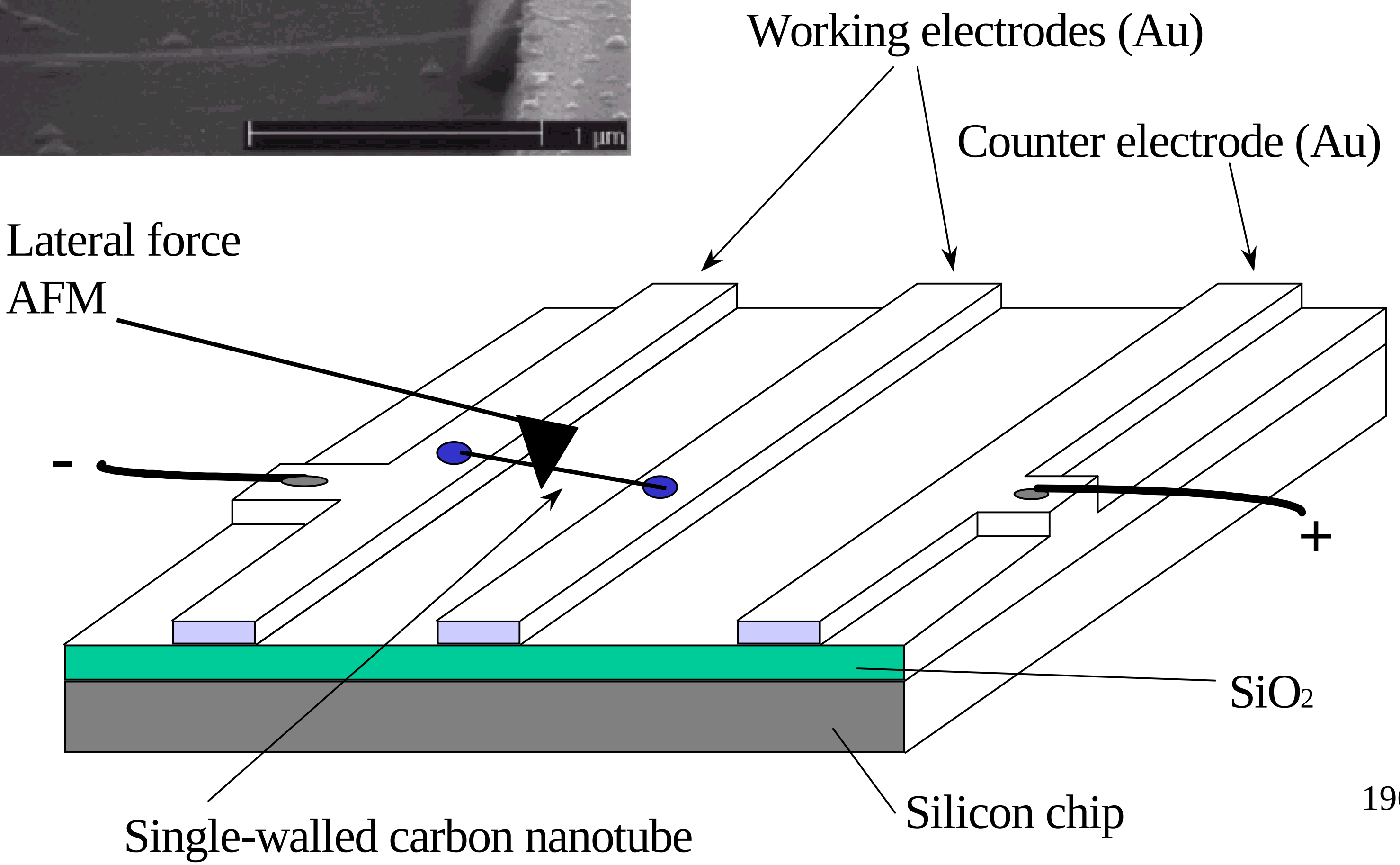
Nanotube 2-D Switch

Present 1-D Switch

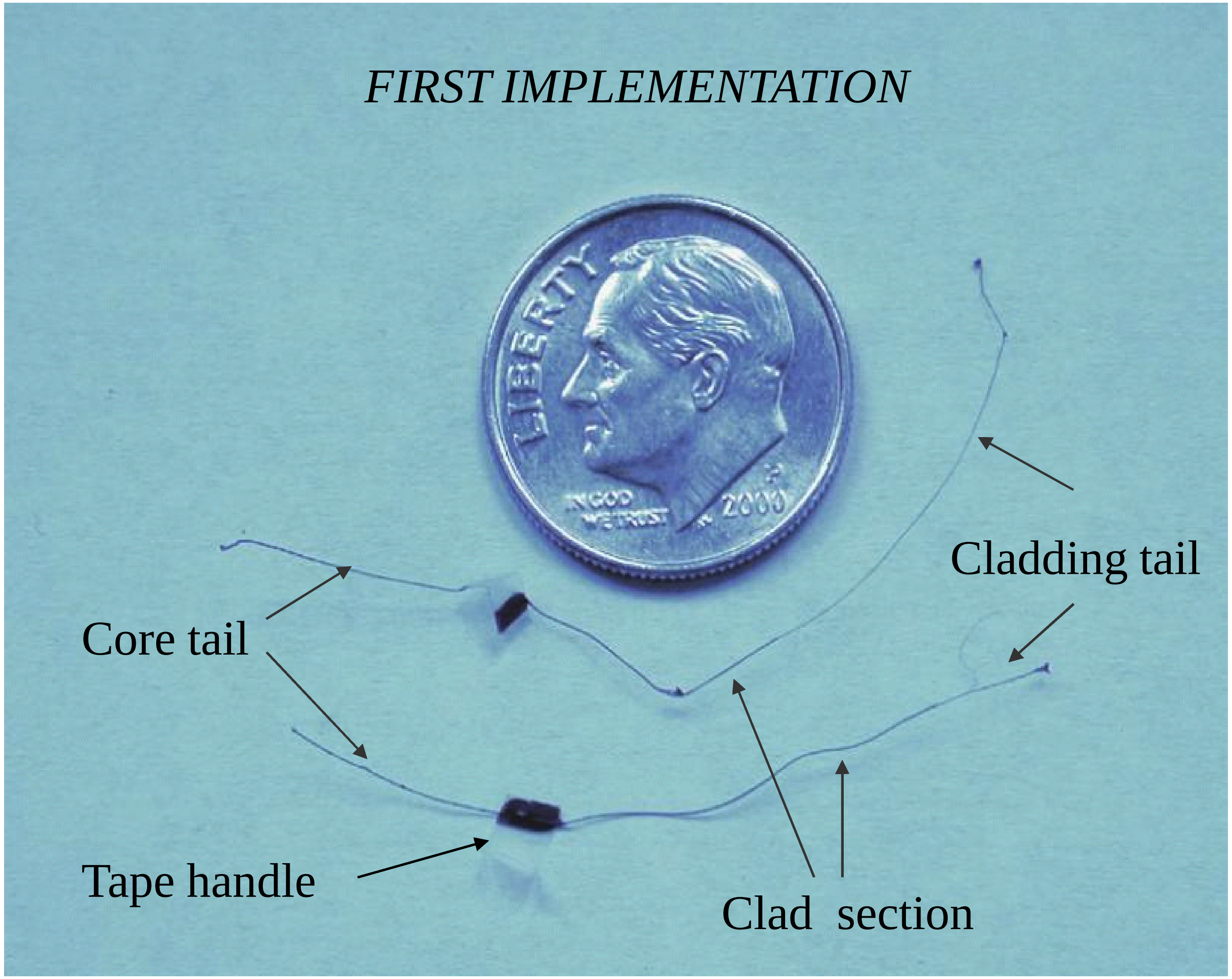
WORLD'S SMALLEST ARTIFICIAL MUSCLE:

Carbon nanotube 1/50,000 the diameter of a human hair





Fiber Supercapacitors For the Energy Sufficient Soldier and Micro-Air Vehicles



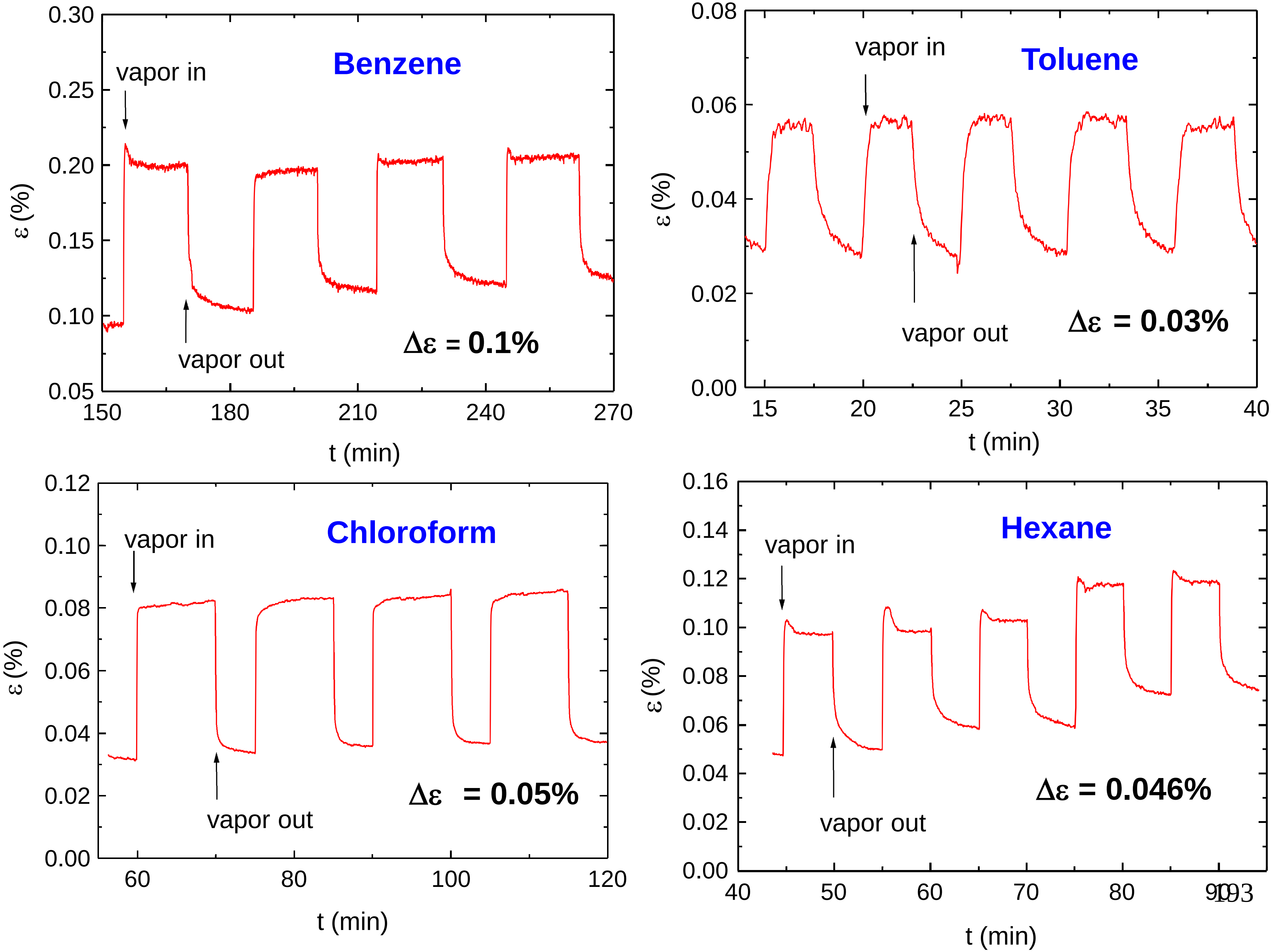
Chemical Actuation: The Basis For Autonomous Sensor/Actuator

Concept: Non-electrical actuator material senses gas concentration and provides appropriate actuator response.

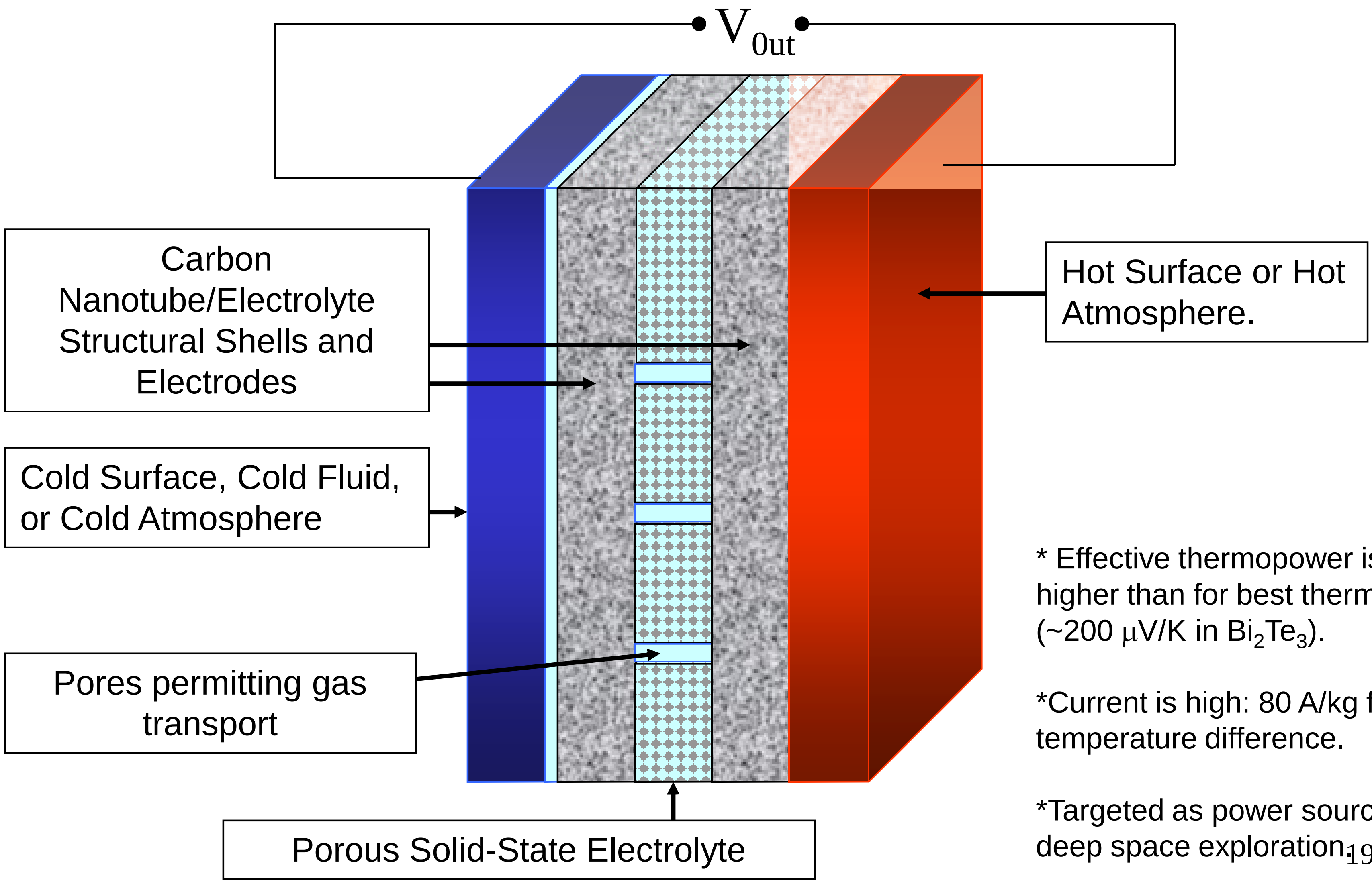
Examples of possible applications:

- Chemical/biological protection clothing comprising arrays of cantilever microvalves.
- Self-regulating microfluidic valves for engines.

Data on Chemical Actuation



Thermal Energy Harvesting Using Carbon Nanotube Composite As A Structural Wall



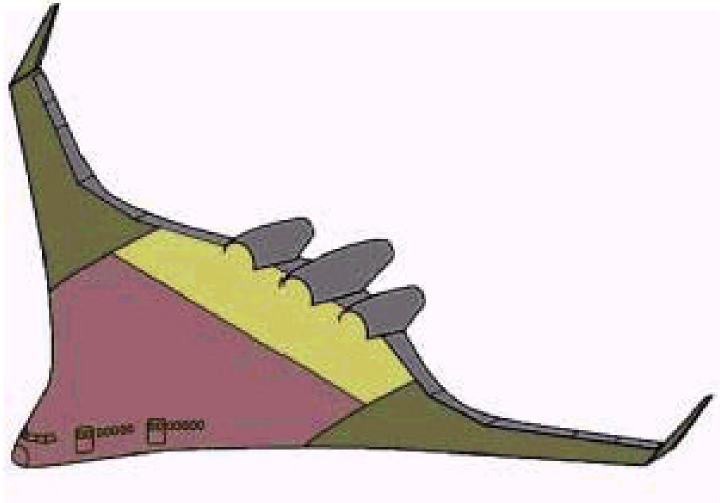
* Effective thermopower is 6X higher than for best thermoelectric (~200 μV/K in Bi_2Te_3).

*Current is high: 80 A/kg for a 60°C temperature difference.

*Targeted as power source for deep space exploration

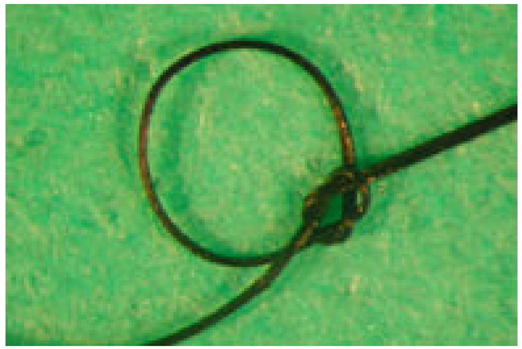
NASA VIEWPOINT

Potential Benefit of Nanotube Composites for the BLENDED WING BODY, ADVANCED LONG-RANGE TRANSPORT CONCEPT



- Simple application of Carbon Nanotube materials cuts the empty weight of the vehicle by 45% and design fuel required by 25%

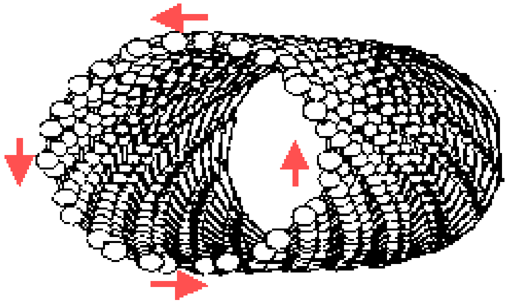
OUR TEAMS SPINNING PROCESS PROVIDES THE STRONGEST KNOWN CONTINUOUS NANOTUBE FIBERS



Technologies of the NanoTech Institute will Lead to Products

Technology Need	Economic Drivers	Specific Requirements
Sensors (navigation, gas, magnetic field, pressure, bio, position, chemical, neural network)	Aerospace, industrial, and home products	Decreased size, increased sensitivity and selectivity, and decreased cost
Thermoelectrics and thermoionics with increased efficiencies	Power systems and cooling for aerospace and home	ZT > 1 over wide temperature range
Low-voltage, high-stroke actuators with high power capacity	Aerospace and industrial control Robotics	High cycle life, energy efficiency, rate, force generation, and (for engines) high temperature stability
Improved electroluminescent displays	Cockpit and computer displays	Improved carrier injection providing increased efficiencies, brightness, and life
Fast, ultra-high density electronic circuitry	High speed computing	Ultra-high speeds, ultrahigh device densities, and low power
Intelligent and multifunctional materials	Advanced DOD and aerospace integrated systems (weight and cost savings from multifunctionality)	High strength nanotube/polyelectrolyte composites with combined structural, actuation and energy processing functions
Microfluidic circuitry	Hydraulic control systems for aerospace, biotechnology, and industrial applications	Microfluidic actuation and sensing Electrowetting driven pumps
Energy harvesting devices (thermal, photo, and mechanical)	Advanced DOD systems Waste energy harvesting for aircraft and in the home	Nanotube/polyelectrolyte microstructures with combined structural and energy harvesting functions
Micro machines	Advanced controls, sensors, and laboratory on a chip	Micromechanical switches for optical fibers
Optical circuitry elements	Sensing, high speed computing, and VCSELs	Photonic-crystal based optical device and interconnect structures
Smaller energy storage devices with higher capacity and faster charge and discharge	Aerospace, industrial, and commercial power systems Energy storage on circuit boards	Low cost, high-cycle-life supercapacitor with C > 300 F/gm and charge time less than 0.1 sec
Gas storage systems	Aerospace, industrial, and commercial power systems	Low cost H_2 storage medium with capacity > 8 wt %
Improved catalysts	Chemical processing technologies	Low cost, high selectivity catalysts
Improved fuel cells (solid oxide and PEM)	Aerospace, industrial, and home power systems.	Low cost modular SOFC with > 1kW/kg Decreased catalyst and cell resistance, long life
Powders for low-cost fabrication of strong parts	Low cost structural parts for aerospace and other applications	Improved mechanical properties and decreased cost for fabricated parts

A Strange Mechanical Property of Chiral Nanotubes: They Rotate When Stretched.



(10, 5) Chiral Nanotube

* Rotation can exceed 900°/micron (10% tensile strain for (4,2) nanotube).

* Rotation for an applied tensile strain goes as (tube diameter)$^{-1}$.

* Direction of rotation is counter-intuitive.

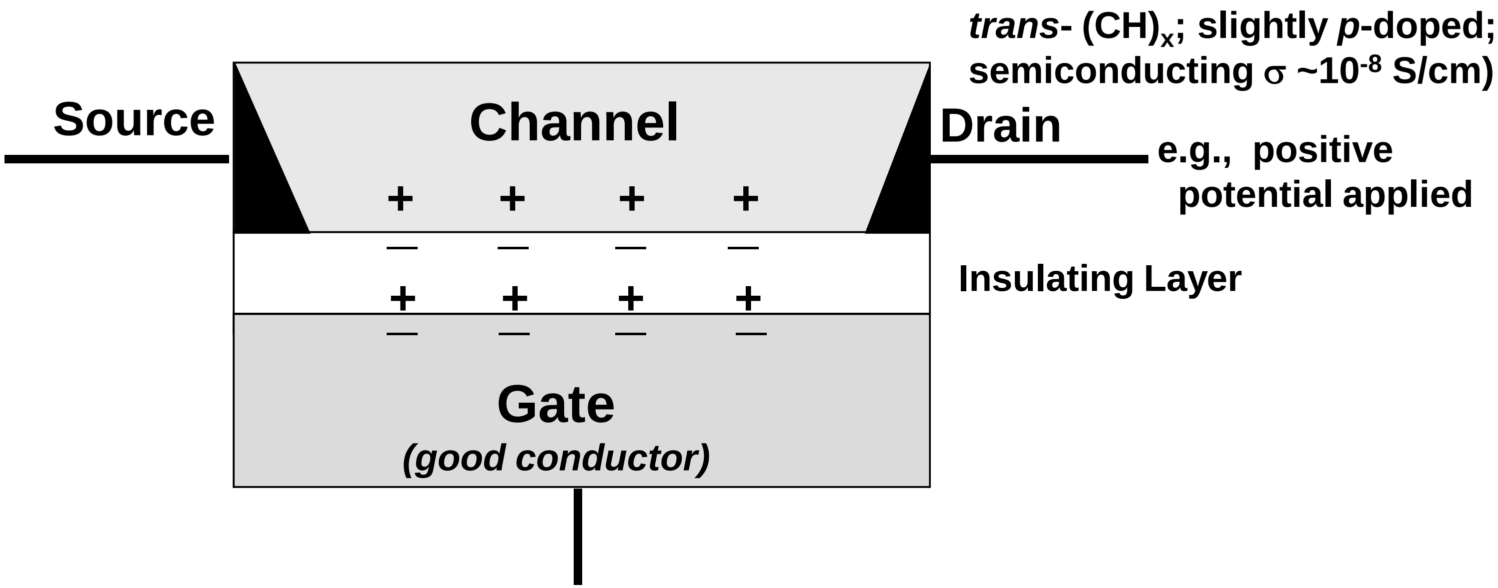
* Energy driving rotation is small relative to total strain energy:

	Tube Type		
Strain (%)	(4, 2)	(6, 3)	(10, 5)
5	0.20%	0.06%	0.05%
10	0.56%	0.16%	0.13%

Santa Claus Illustrates This Effect!

Charge Injection Doping*

(No dopant ions involved)



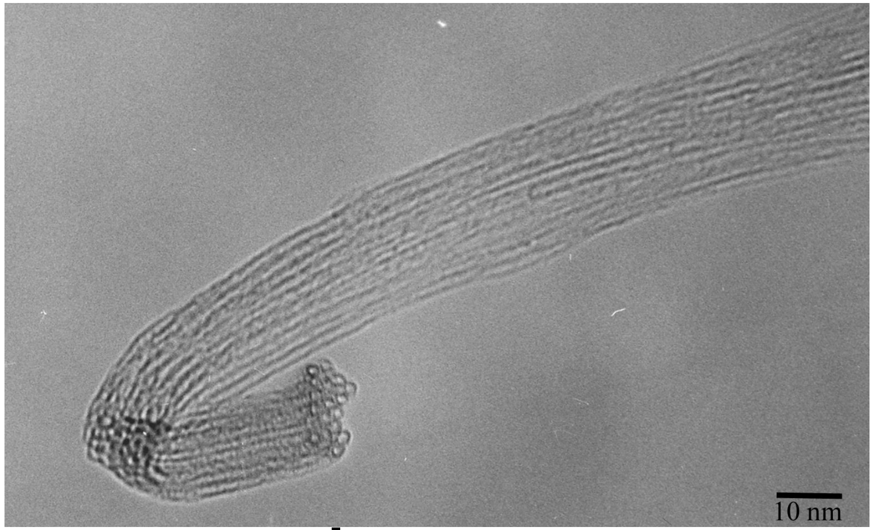
<u>Under the influence of an applied electric field:</u>

See spectroscopic signature characteristic of solitons which disappear on removal of field.

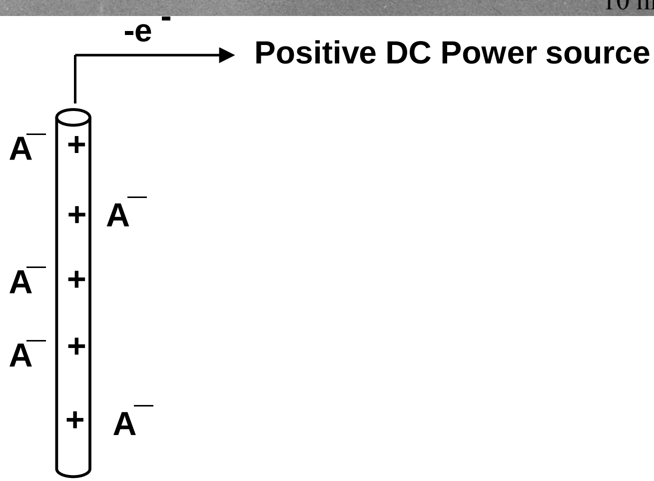
Increase in conductivity by a factor of ~2000 when V_g changed from +5V to -30V.

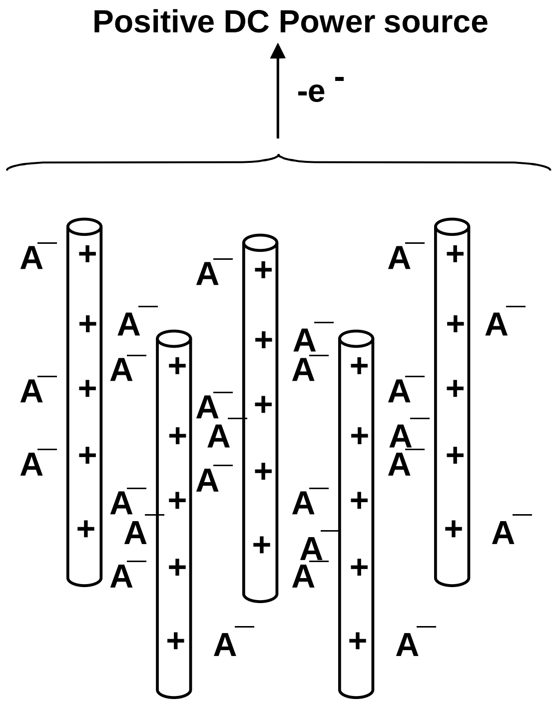
(no dopant ion present; therefore, one can observe the intrinsic conductivity with no complication from coulombic effects between charged polymer chain and dopant)

* J.H. Burroughs, R.H. Friend, P.C. Allen, J. Phys. D.: Appl. Phys. **22**, 956 (1989); K.E. Ziemelis, et al., Phys. Rev. Lett. **66**, 2231 (1991). See also: C.T. Kuo et al., Synth. Metals **88**, 23 (1997): Synth. Metals **88**, 102 (1997).



Single-Walled Carbon Nanotube (SWNT) Bundles*





Single Tube

- **Anions on surface**
- **Remove D.C. source?**
- **Capacitance effect**

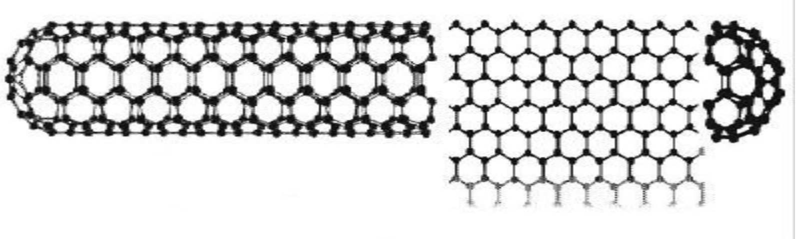
Bundle

- **Anions also inside a bundle**
- **Remove D.C. source: charge on tubes in bundle remains, e.g. $(CH)_x$**
- **Faradaic effect**

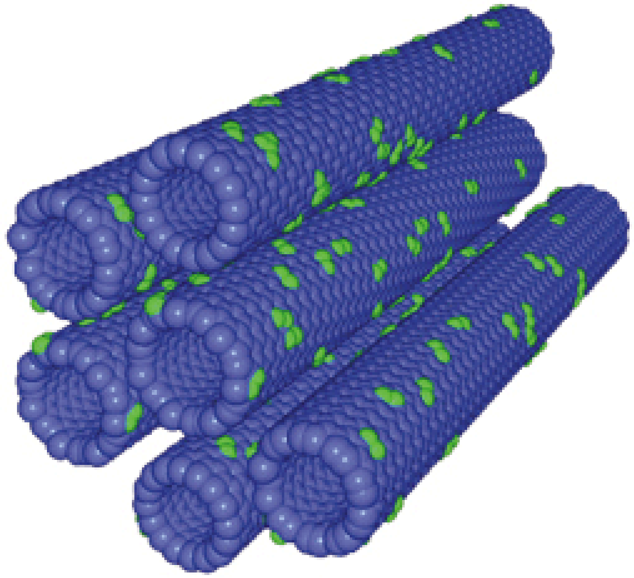
Is there a real difference? (semantics?)

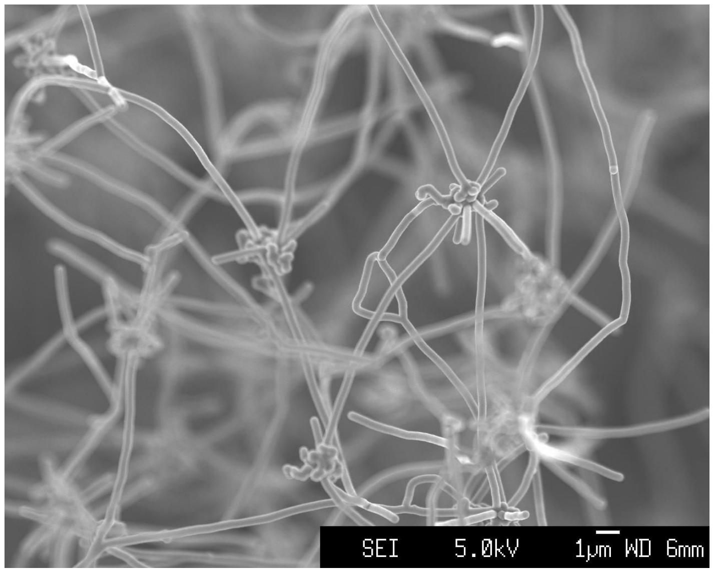
**Reproduced from E. Munoz, Ph.D. Thesis, Instituto de Carboquimica (CSiC), Saragoza, Spain, 2000.*

Single-walled Carbon Nanotube
(diameter ~1nm)

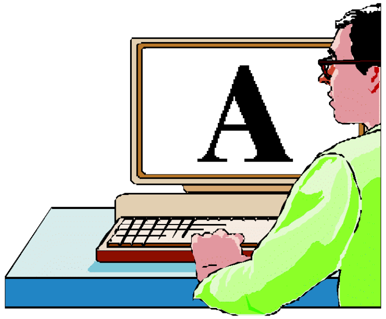


Single-walled Carbon Nanotube Bundles



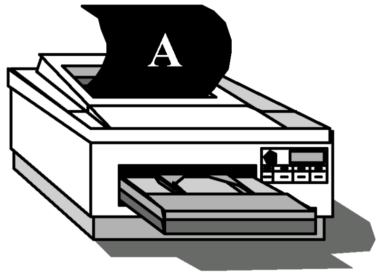


What is "Line Patterning" ?

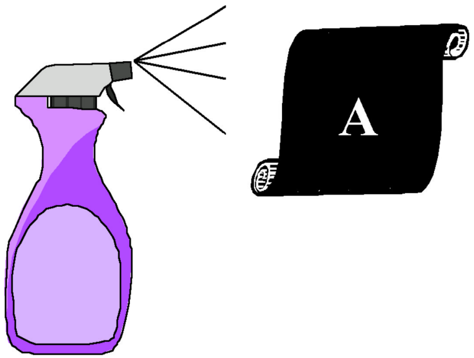


(1) Design

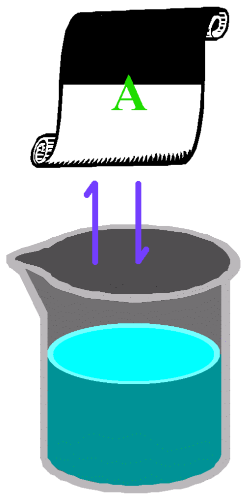
Inversion



Printing



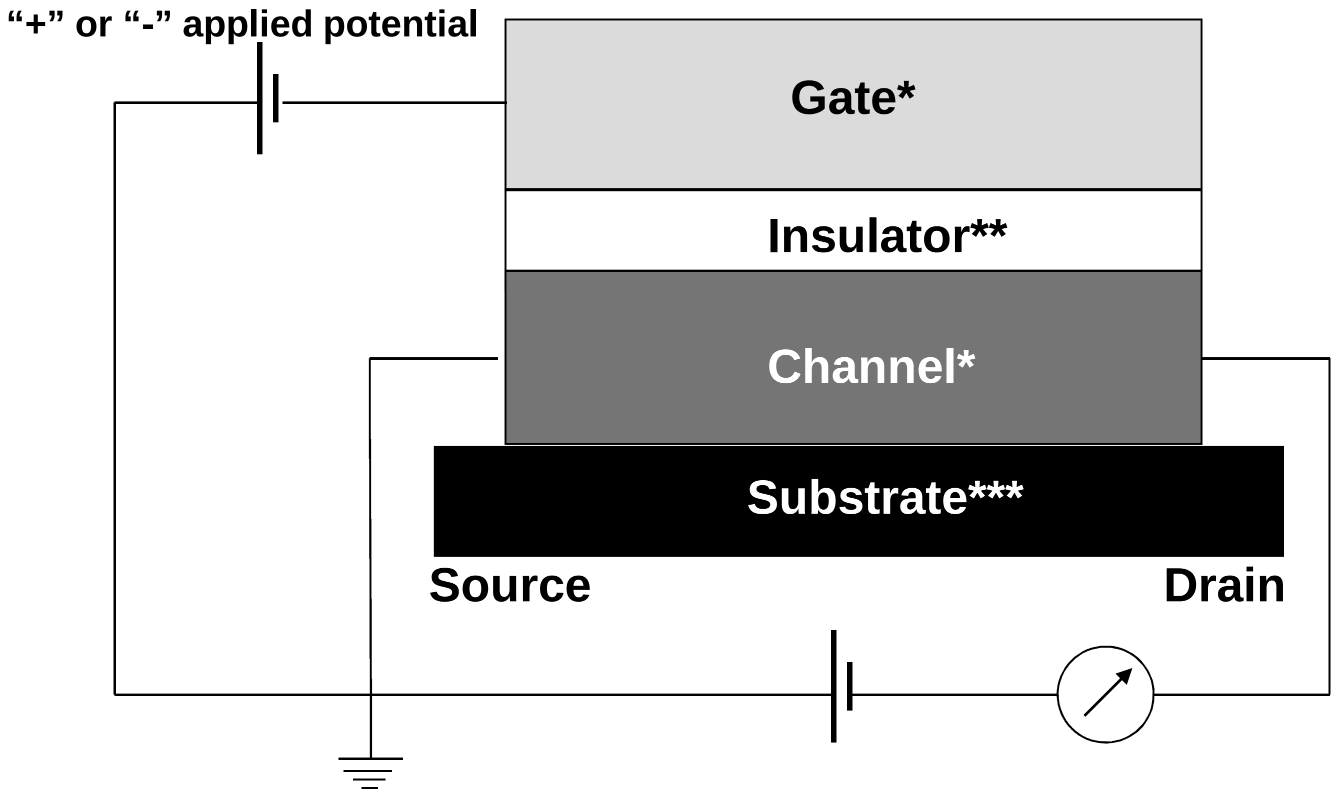
(2) Coating with
conducting polymer



(3) Removal of printing

FET Device Constructed Entirely from SWNT Bundles

(channel is highly conducting, σ ~ 54S/cm)

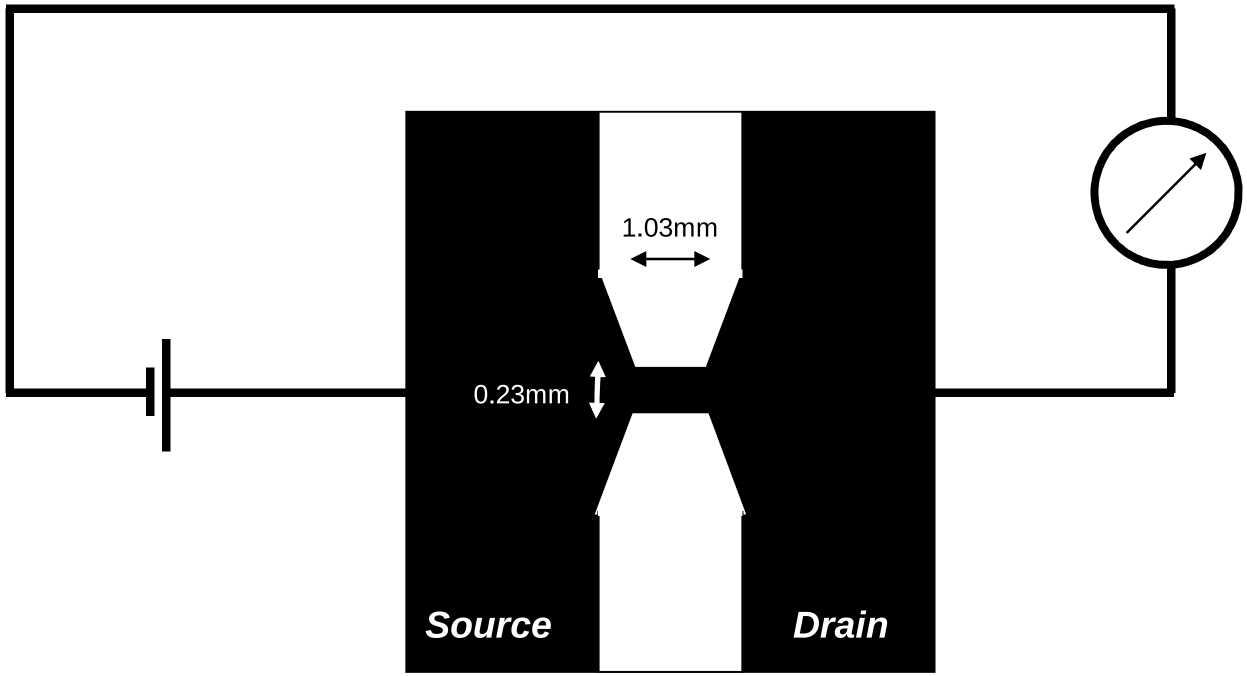


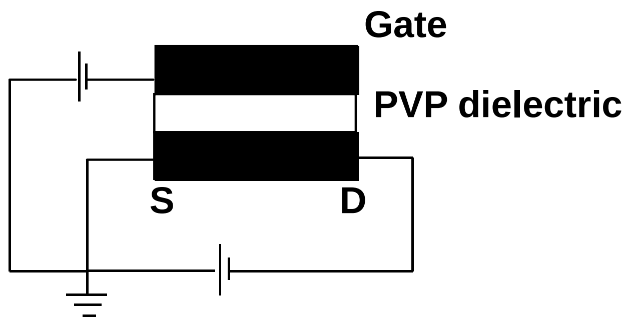
*** Appx. 225nm thick film of laser-oven produced SWNT bundles (~25nm diameter; semiconducting and metallic).**

****Appx. 400nm thick film of polyvinylphenol (spun cast).**

*****Plastic substrate, polyethylene terephthalate ("overhead transparency").**

Single-walled Carbon Nanotube Bundles Field-Effect Device *(top view)*

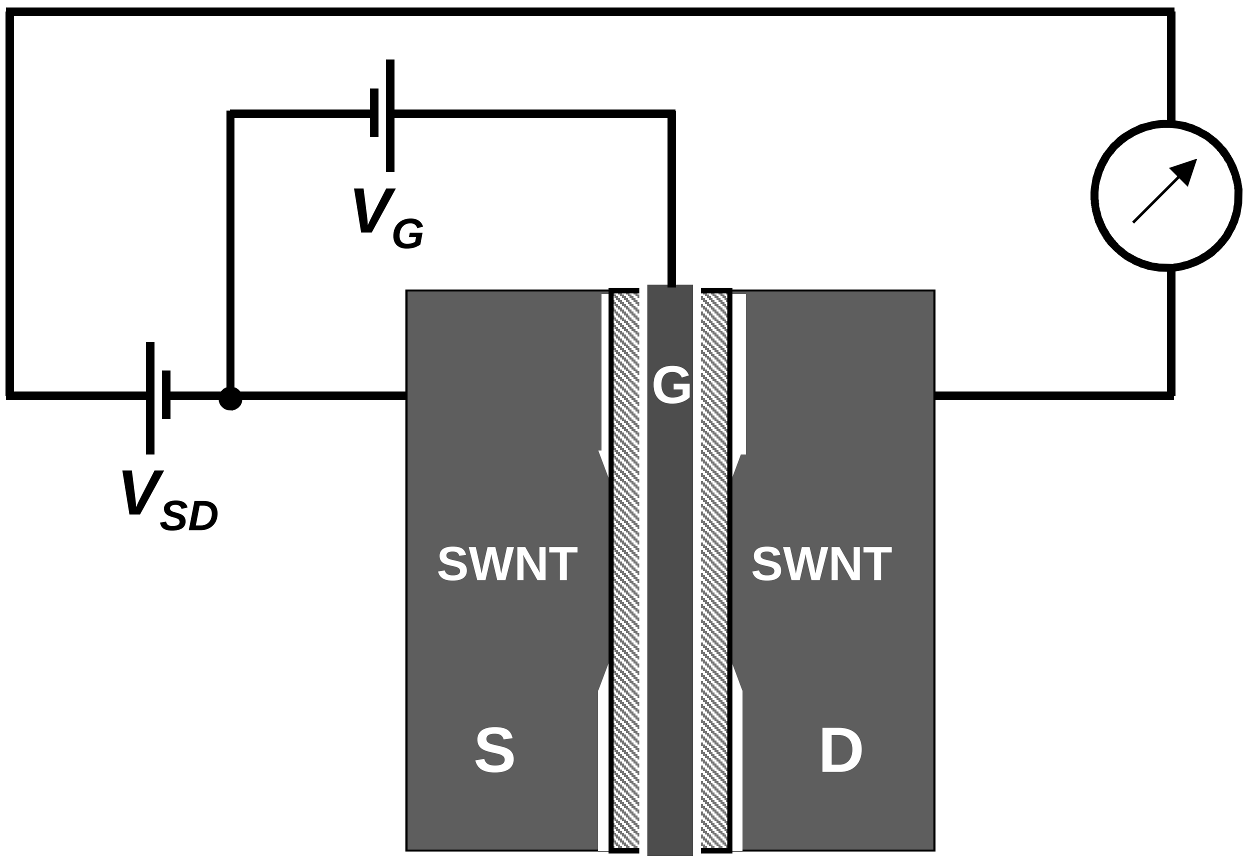




■ = Conducting SWNT bundles coated on PET

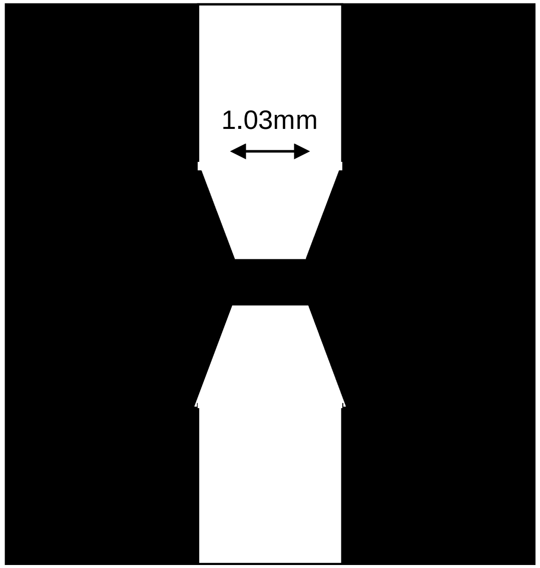
□ = PET substrate

Single-walled Carbon Nanotube Bundles Field-Effect Device *(top view)*

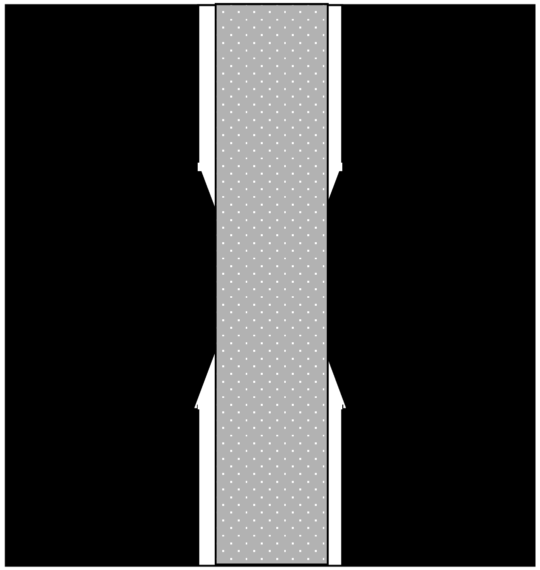


Field-Effect Device made from Single-walled Carbon Nanotube Bundle *(channel & gate)*

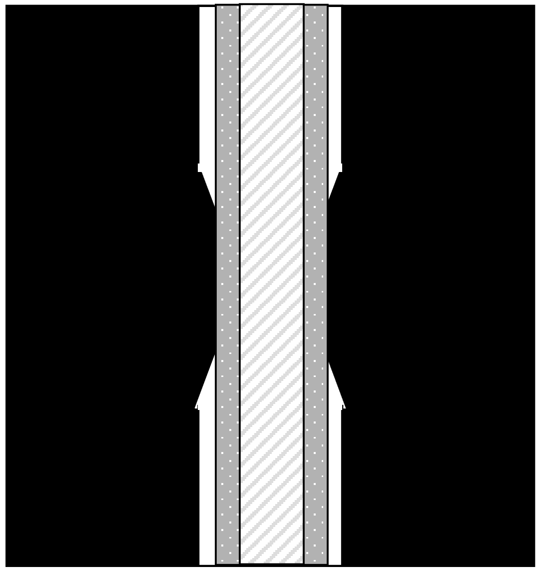
(Produced by Line Patterning on Plastic Substrate (PET)*



<u>Step-1:</u>
Line-Pattern thin film of SWNT (~225nm) on PET substrate (overhead transparency)



<u>Step-2:</u>
Spin coat PVP ~400nm) from 10wt% solution in isopropanol

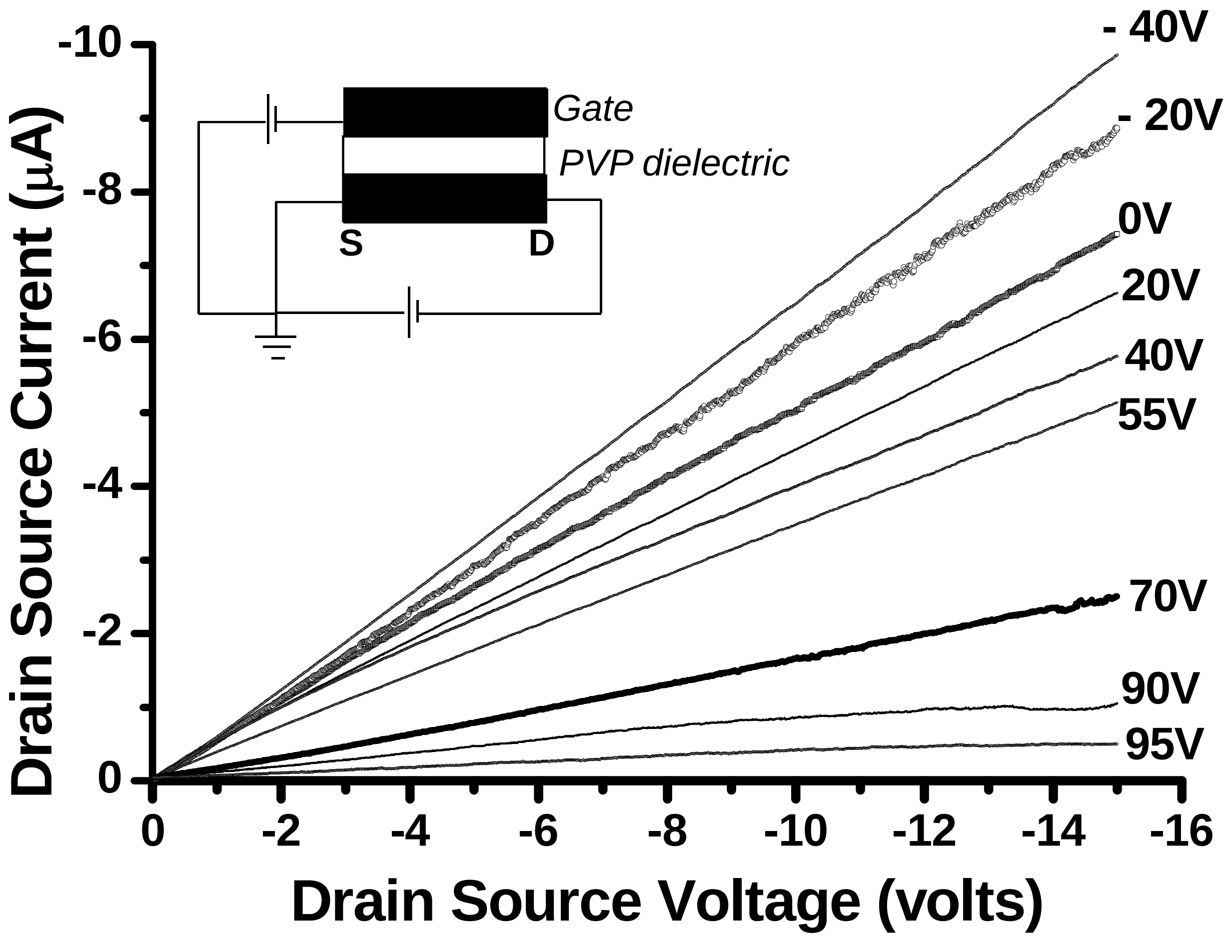


<u>Step-3:</u>
Spin coat SWNT from an aq. dispersion in surfactant

= Source and Drain: SWNT bundles
= Insulating PET (substrate)
= PVP dielectric
= Gate: SWNT bundles

MacDiarmid and Hohnholtz, 2001.

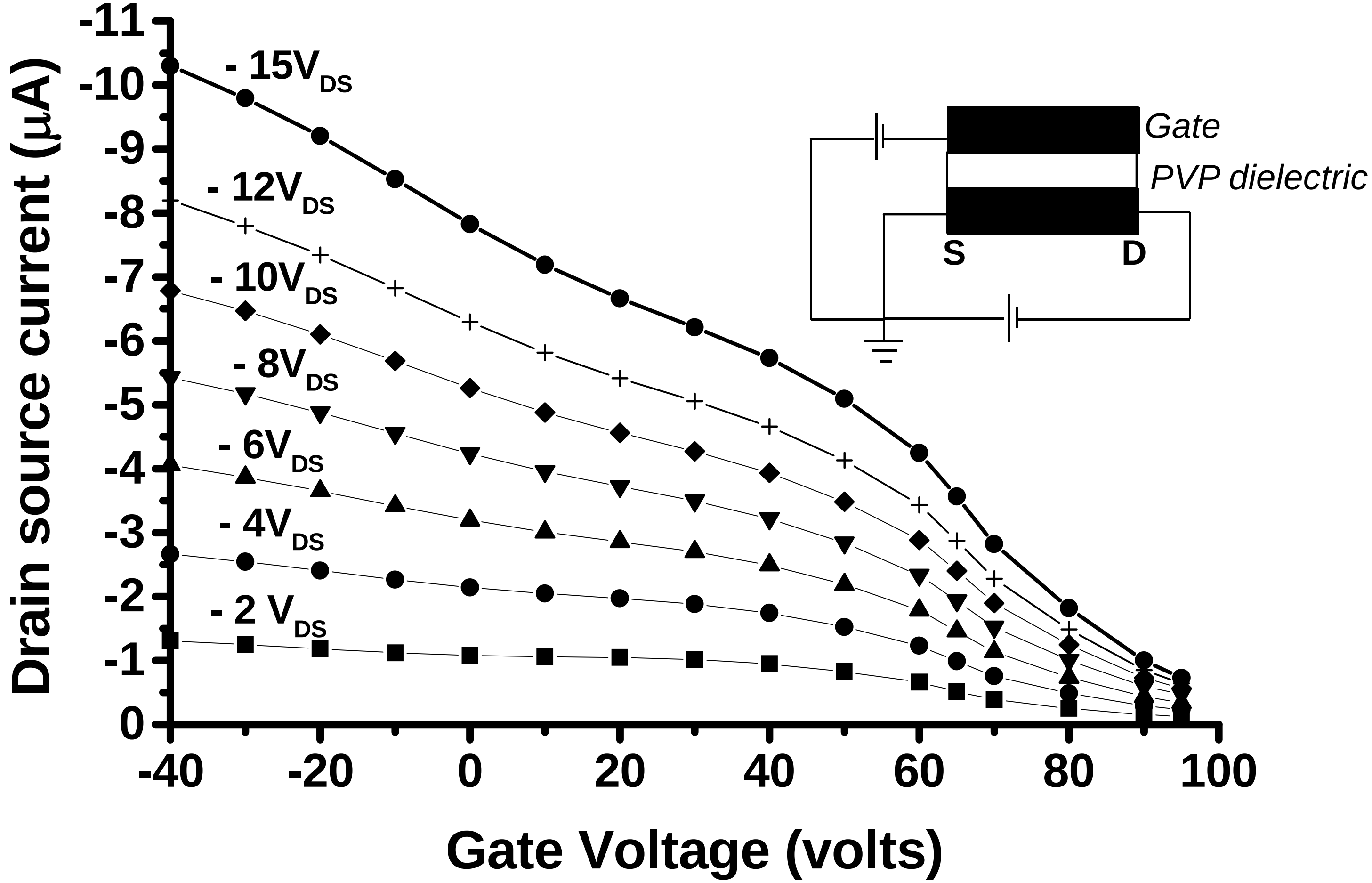
Characteristics of a Transistor Utilizing a SWNT Gate and Channel *(on PET)*



Results consistent with p-type carriers*

Martel et al., Appl. Phys. Lett.* ***73**, 2447 (1998).*

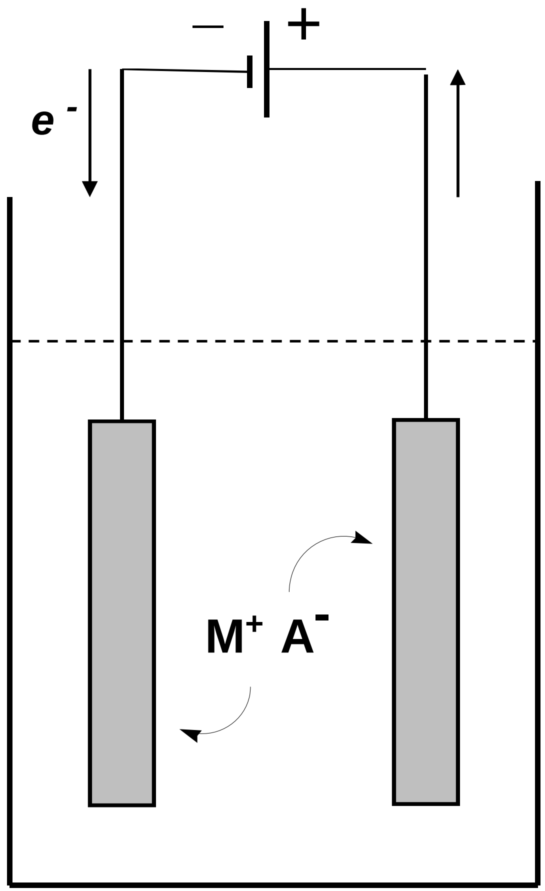
Characteristics of a Transistor Utilizing a SWNT Gate and Channel *(on PET)*



Results consistent with p-type carriers*

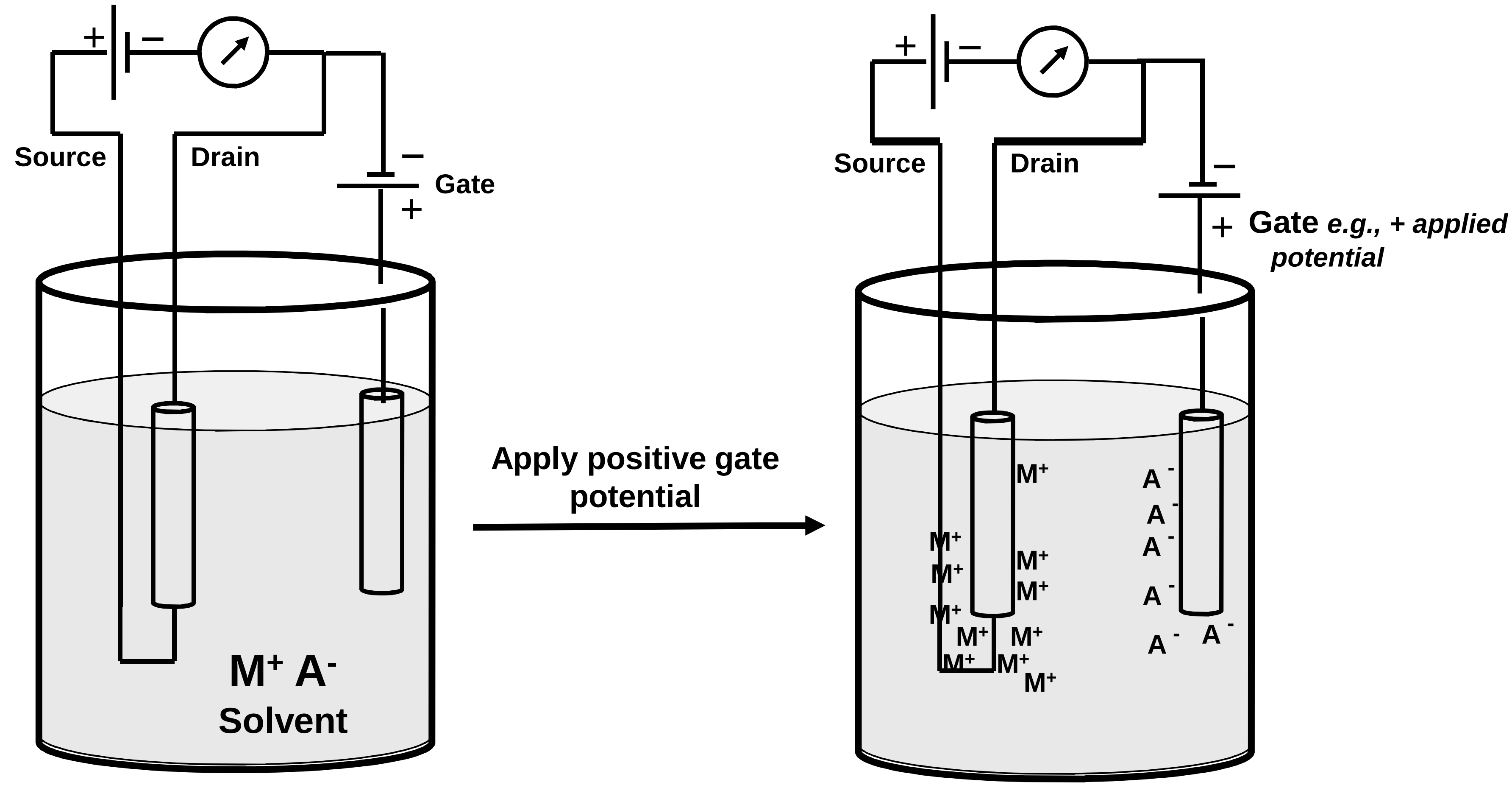
Martel et al., Appl. Phys. Lett.* ***73**, 2447 (1998).*

Migration of Ions in an Applied Electric Field



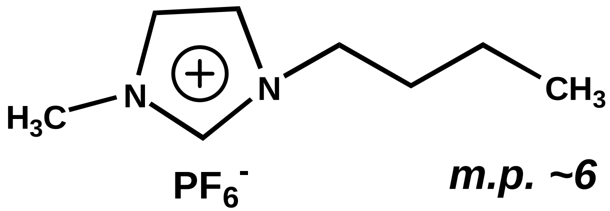
M^+ A^- dissolved in polar solvents

Double-layer "Electrolyte-Gated" Transistor Using SWNT "Gate" and Channel



$M^+ = (Bu_4N)^+$; $A^- = (BF_4)^-$

Solvent = CH_3CN, <u>or</u> a RT molten salt. e.g.,



m.p. ~6 ^{o} C

Assume: M^+ and A^- ions do not enter the bundle

Transparent Conductors

eikos INC.

Product Development Specialists

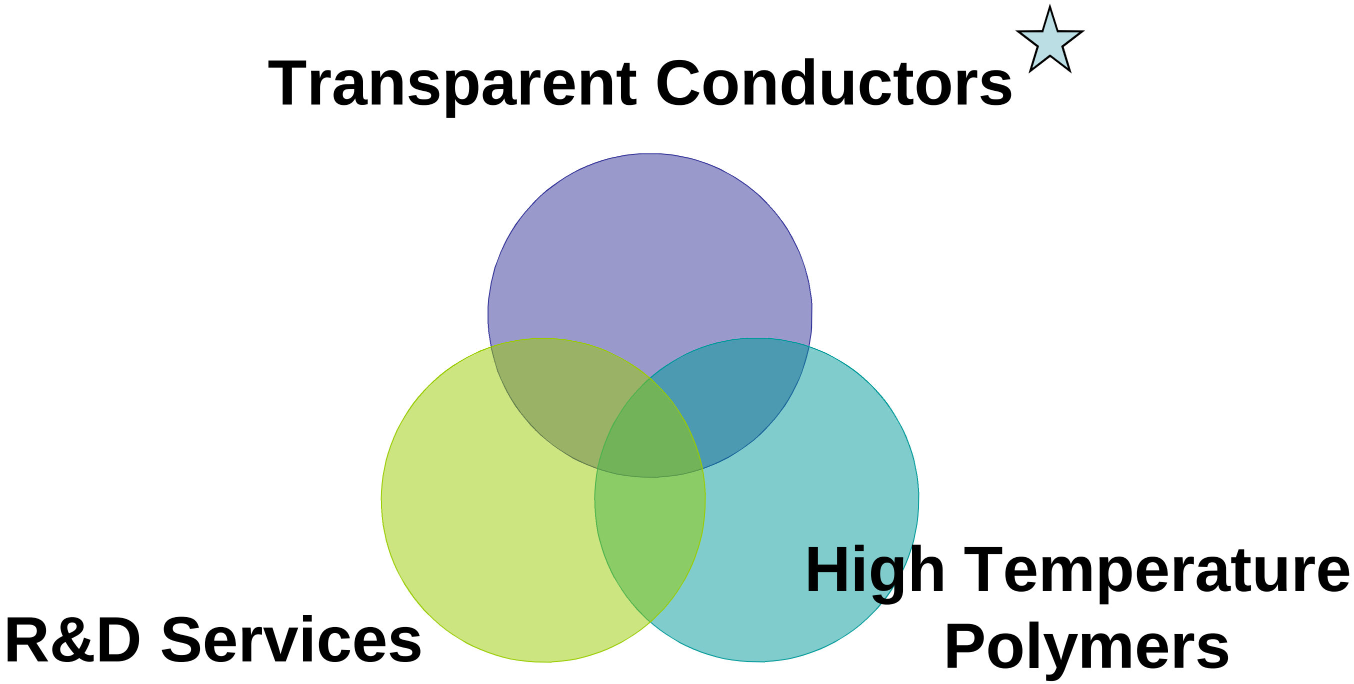
Eikos, Inc.

- Product Development Specialists
  - Nanocomposites
  - High Temperature Polymers
- Founded in 1996 (private company)
- Located in Franklin, MA
- 14,000 ft^2 Facility
- 10 Employees

Management

- Joe Piche, CEO & Founder
  - BS, Polymer Chemistry
  - 20+ yrs exp. in Specialty Materials
- Dave Arthur, COO
  - BS, MS Chem. Eng., MBA
  - 20+ yrs exp. commercializing technology
- Paul Glatkowski, VP Engineering
  - BS, Chem. Eng.
  - 15+ yrs exp. in Specialty Materials
- Dr. Philip Wallis, Technical Director
  - PhD, Surface Chemistry
  - 20+ yrs exp. with Ink formulations & Ink Jet printing

Three Business Units



Markets

- Military Transparencies
- Touch Screens
- EL Lamps
- Flat Panel Displays
- Window Films
- Plastic ICs (RFID tags, Smart cards, etc.)
- Solar Panels
- Interactive Electronic Textiles

Total Available Market ~ $1 Billion

Products

- Inks
- Films
- Circuits

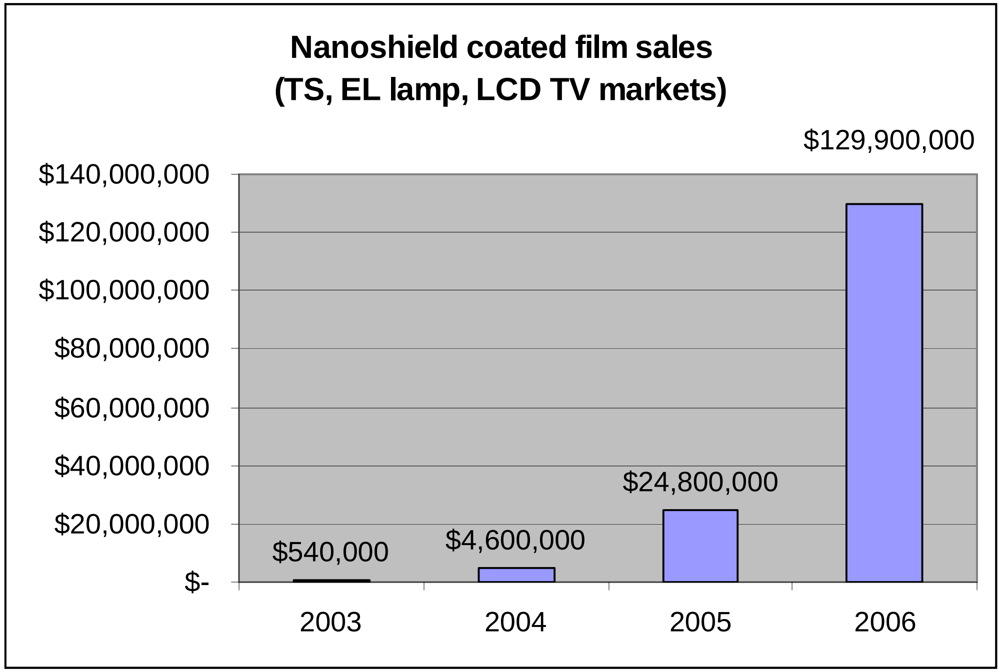
	Product Formats		
Market Segments	Inks	Films	Circuits
Military Transparencies	○	○	
Touch Screens		○	○
EL Lamps		○	○
Flat Panel Displays	○	○	○
Window Films		○	○
Plastic ICs	○	○	
Solar Panels		○	○
Interactive Electronic Textiles	○		

Business Model

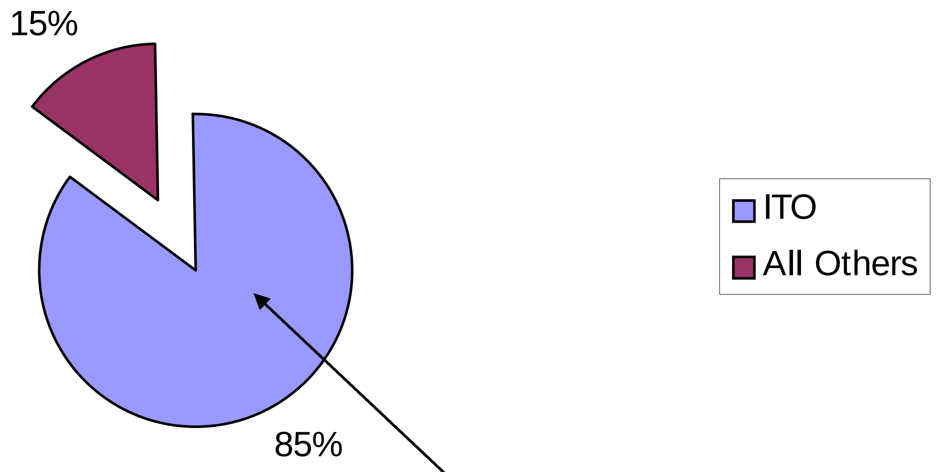
- Produce ink in Franklin, MA.
- Use certified coaters to produce film.
  - Sell film through alliance partners.
  - Offer limited exclusivity based on product format, market segment & geographic territory.
- License digital printing technology to large circuit component manufacturers.
  - Sell ink to licensees and collect royalties.

Sales Forecast (Films)

- Assumptions:
  - 17% market penetration by 2006 (conservative)
  - $2 / ft^2 ASP for coated film
  - Does <u>not</u> include royalty revenues or ink sales.
  - Does <u>not</u> include film sales to other market segments.



Technology Share



Dominated by ITO

(Indium Tin Oxide)

Market Need (vs. ITO)

- Lower Cost
  - Low Capital Costs
  - Coating < \$1 per ft^2
- More Flexible
- Less Color (not yellow)
- Digital Printing capability

The Approach

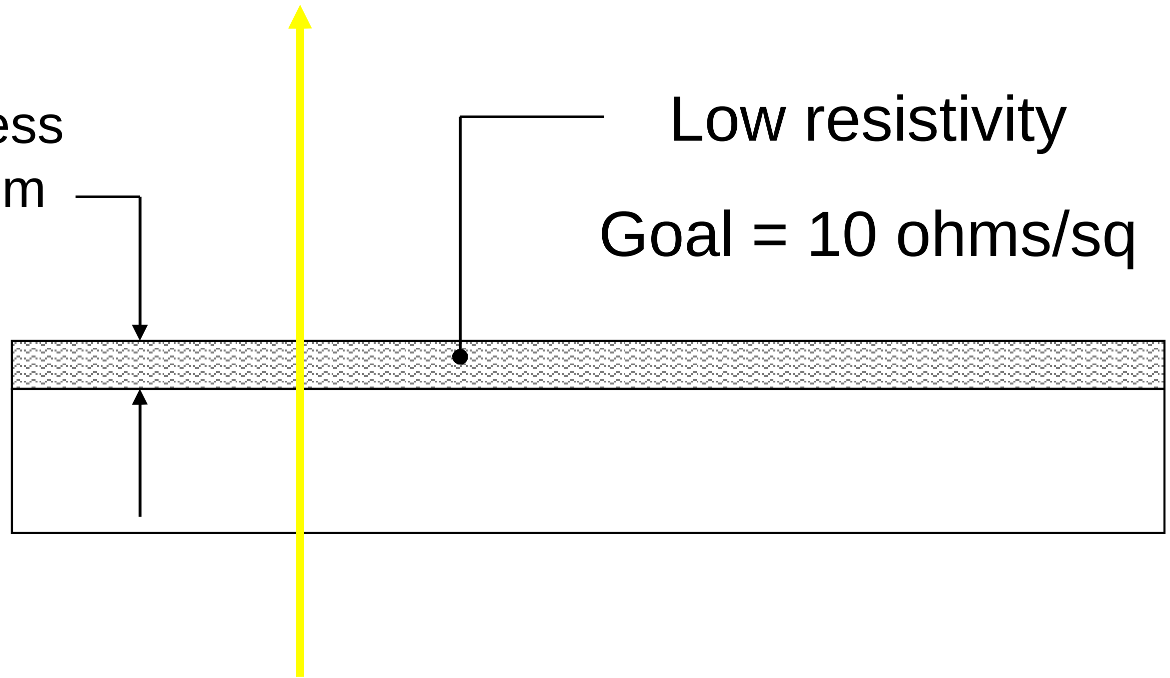
- Transparent Conductive Ink
  - Carbon Nanotube (CNT) “Pigment”
  - Polymer “Binder”
  - Solvent Based
- Tailored Formulations
  - Transparency / Resistivity - CNT
  - Mechanical Properties - Binder

ITO Killer:
Transparent Conductive Ink

Thickness
< 100 nm

Low resistivity

Goal = 10 ohms/sq



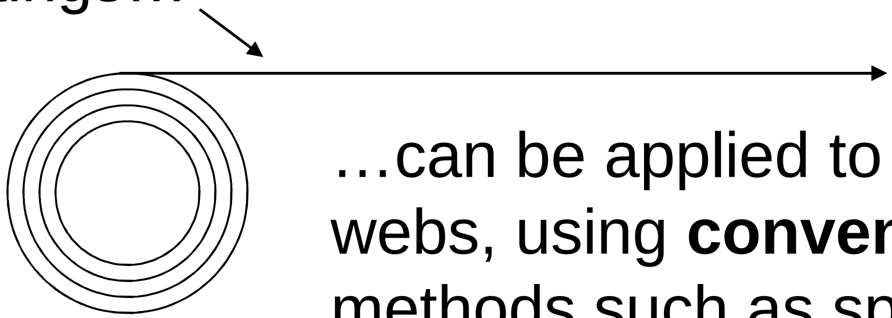
High visible light transmission

Goal > 90%

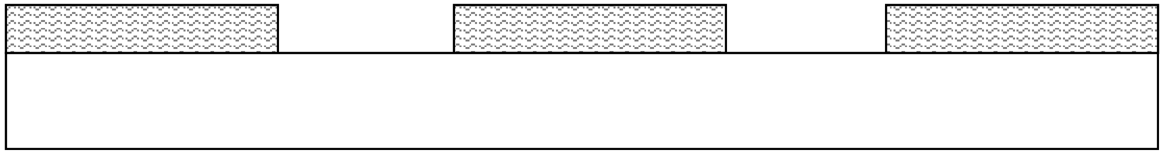
*** Patents Pending**

Ease of processing advantage!

CNT coatings…



…can be applied to continuous webs, using **conventional** methods such as spraying, dipping, knife coating, etc.



Circuits can also be **directly printed *** using screen or ink jet printing!

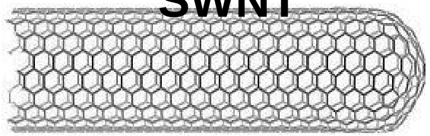
*** Patents Pending**

Carbon Nanotubes

- High conductivity
  - 3×10^{-5} ohm-cm (SWNT ropes)
- Small size & High aspect ratio
  - 1 nm diameter
  - L/D > 1,000
- High stability
  - UV, Temperature, Humidity, Solvents
- Self Assembly characteristics

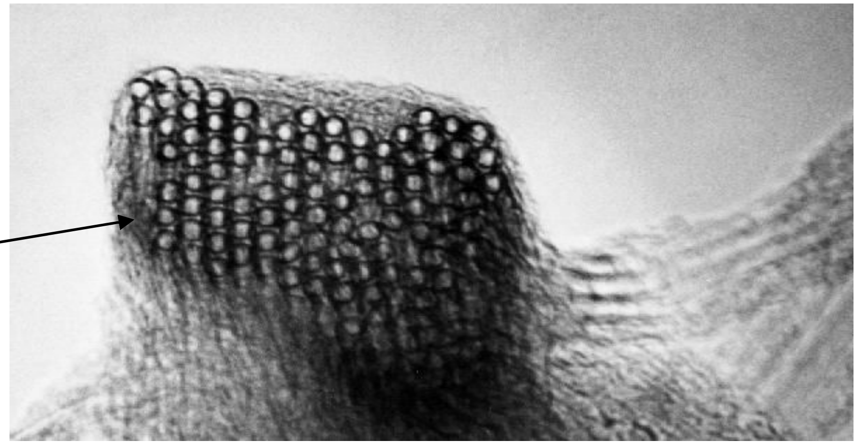
Single-Wall Nanotubes (SWNT)

SWNT



D ~1 nm, L/D > 1,000

Self Assembly: SWNT ropes



Nanoshield^{TM} Ink

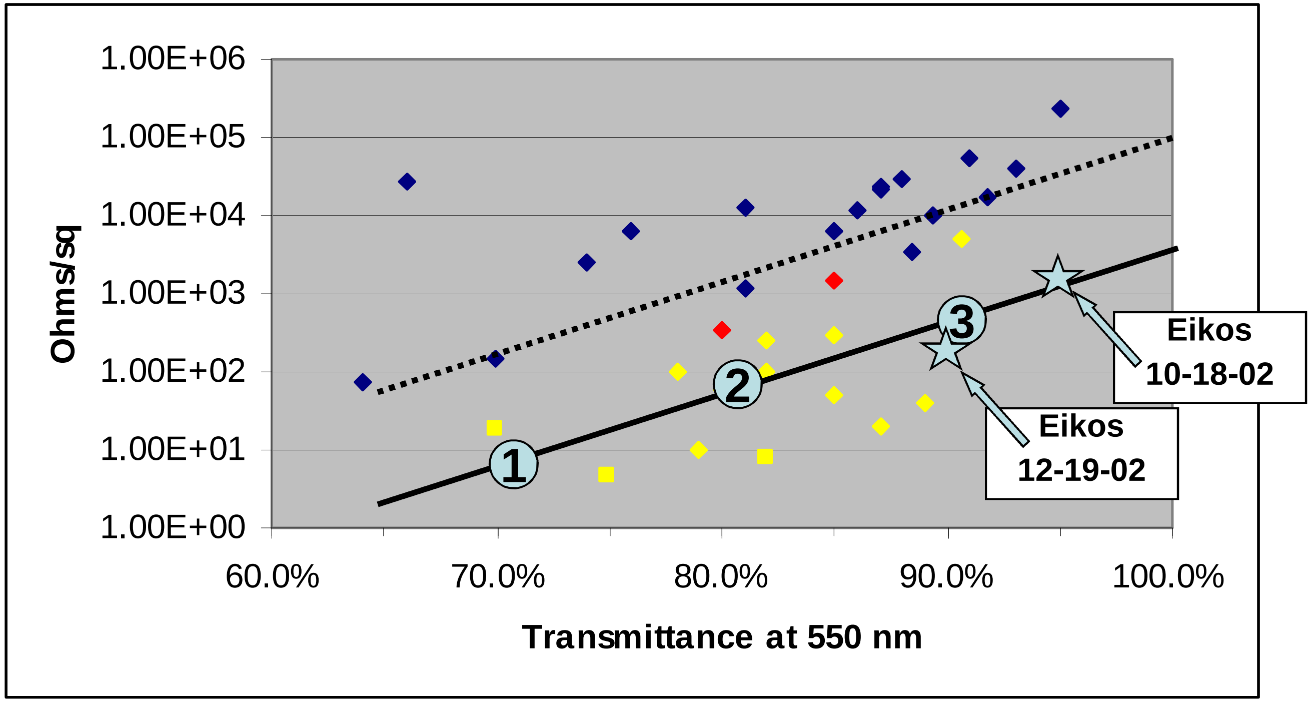
ITO Killer!

Target Applications

1 **EMI / LO**

2 **FPD**

3 **TS**



Eikos (July'02)

Sputtered ITO

ICP (PEDOT)

Sputtered Ag or Au

Transparent Conductors
233 ohms/sq @ 90% transparency!

Nanoshield™ coated PET film

Competitive Approaches

	CNT dispersions	Sputtered ITO	Spray Pyrolysis	ITO dispersions	ICP dispersions
Transparency	○	○	○	◉	○
Conductivity	◉	○	○	●	◉
Cost	○	●	○	○	◉
Compatible with plastic substrates	○	○	●	○	○
Ease of patterning circuits	○	●	●	◉	○
Flexibility / ductility	○	●	●	●	○
Environmental stability	○	◉	◉	◉	◉
Compatible with 3D substrates	○	●	●	○	○

○ Excellent
◉ Good
● Poor

Superior cost / performance

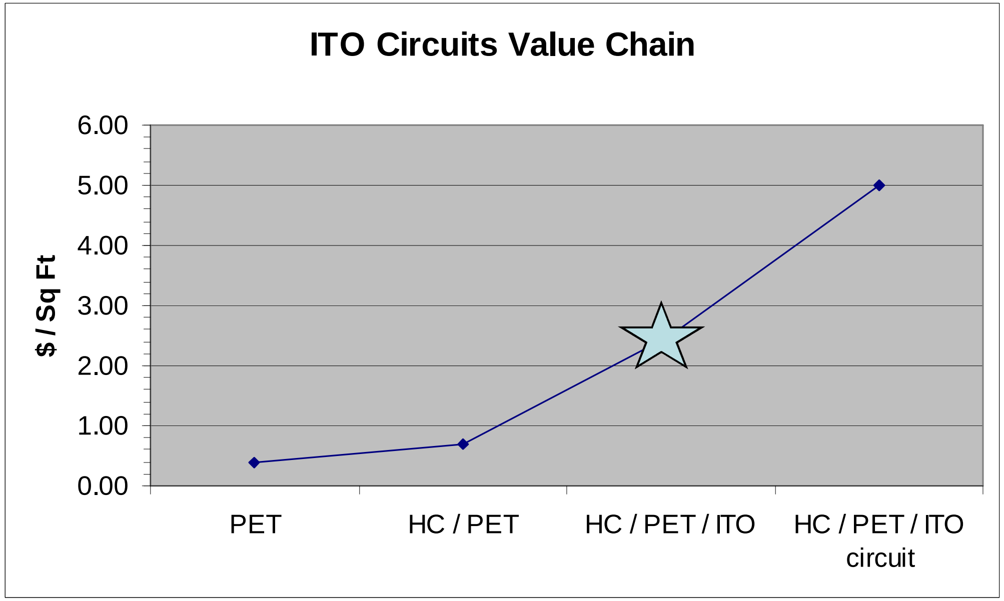
Intellectual Property

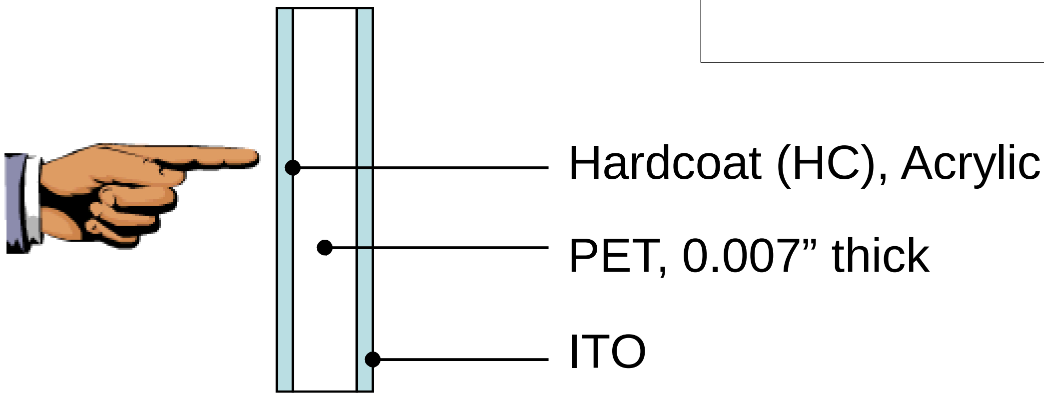
- **Issued Patents:**
  - Electromagnetic Shielding Composite Comprising Nanotubes**.**
    - US Patent 6,265,466 issued July 2001
- **Other Patents Pending (US & PCT applications filed):**
  - ✓ Transparent Coatings Comprising Carbon Nanotubes and Methods for Forming the Same.
  - Nanocomposite Dielectrics.
  - EMI and Lightning Protection Using Carbon Nanotubes.
  - Polymer Nanocomposites and Methods for the Preparation Thereof.
  - Conformal Coatings Comprising Carbon Nanotubes.
- **"Key" US Provisionals Filed:**
  - ✓ Patterning Circuits from Carbon Nanotube Dispersions.
  - ✓ Highly Optical Transparent Nanostructured Electrical Conductors.
  - Mixtures of Carbon Nanotubes and Other Conductive Fillers.

Market Research shows High Interest!

- 3M MicroTouch
- Army Research Labs
- Cambridge Display Tech.
- Dupont - Polar Vision Inc
- Durel Corporation
- E Ink
- Elo Touch Systems
- Gyricon
- Dr. Leuder
- Dr. Gregory Crawford
- Dr. Robert Pinnell
- Kent Displays
- Kodak Displays
- LG Philips
- NEC
- Optrex
- Plastic Logic
- Sharp
- Sony
- Tekra
- Toppan
- Toshiba
- Touch International
- Universal Display Corp.
- Vitex
- Viztec

Touch Screens / EL lamps

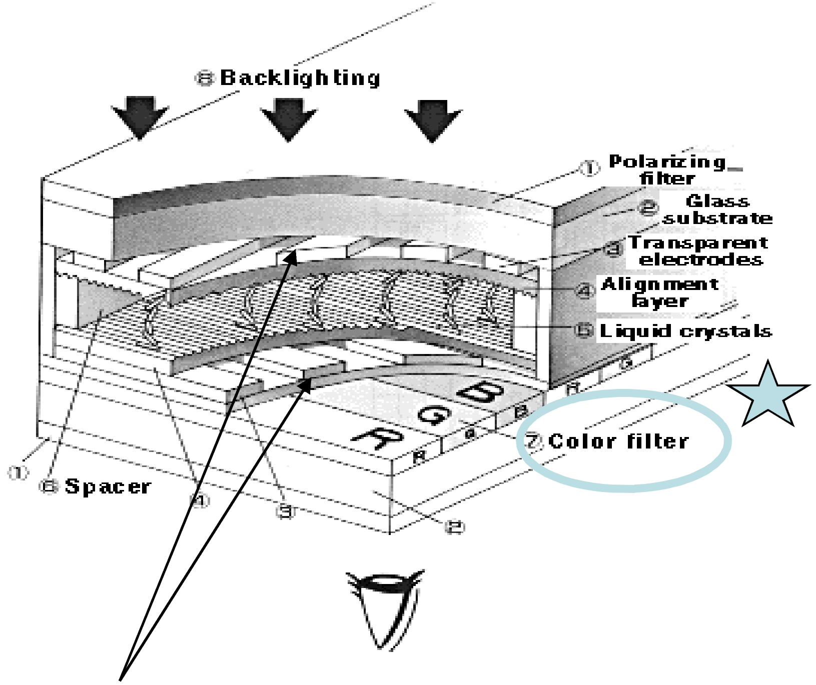




Flat Panel Displays

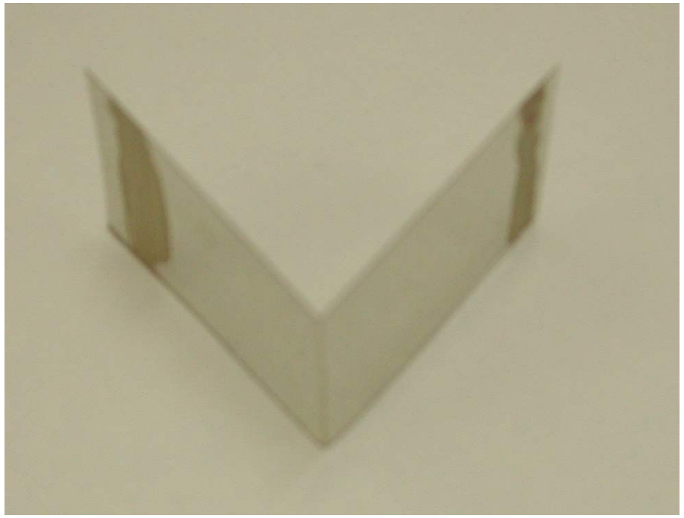
Large LCD TVs

Samsung announces world's first 40-inch TFT-LCD TV.



Transparent electrodes are a critical component in FPDs.

Flexible displays!



- OLEDs
- Electronic paper (E-Ink)

Even after folding and creasing, the resistance of above Nanoshield™ transparent circuit increased less than 5%.

When **ITO** circuit was folded, the result was an **open circuit**.

Nanoshield™ Transparent Conductors

- ☑Differentiated Technology
- ☑Technology has been Validated
- ☑IP protected with Patent Filings
- ☑Large Growth Markets
- ☑Clear Market Entry Strategy
- ☑Strong Customer Interest
- ☑Solid Team