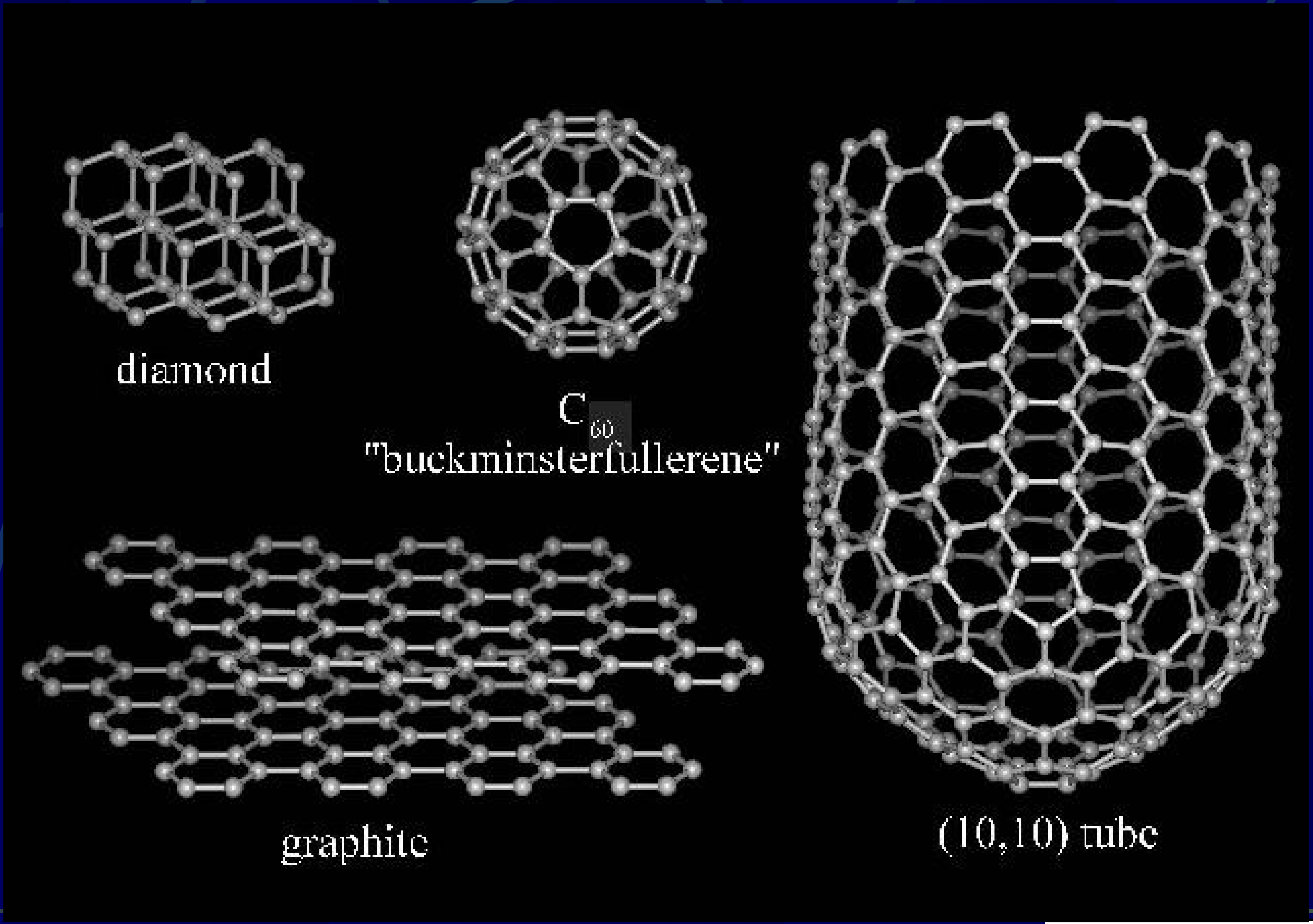
Carbon Allotropes



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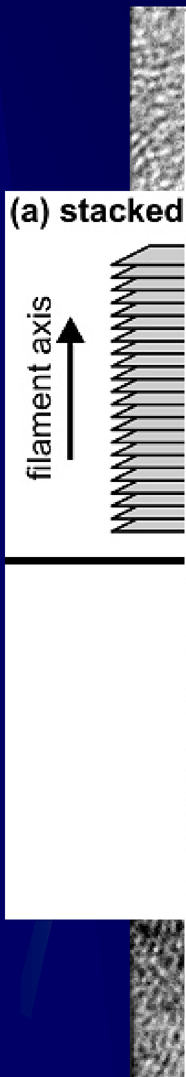
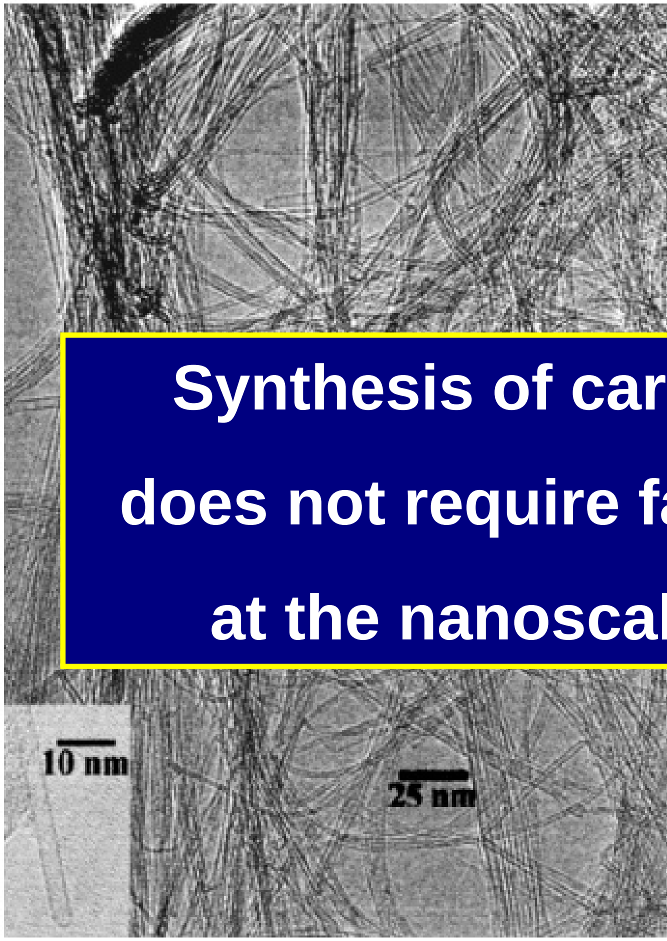
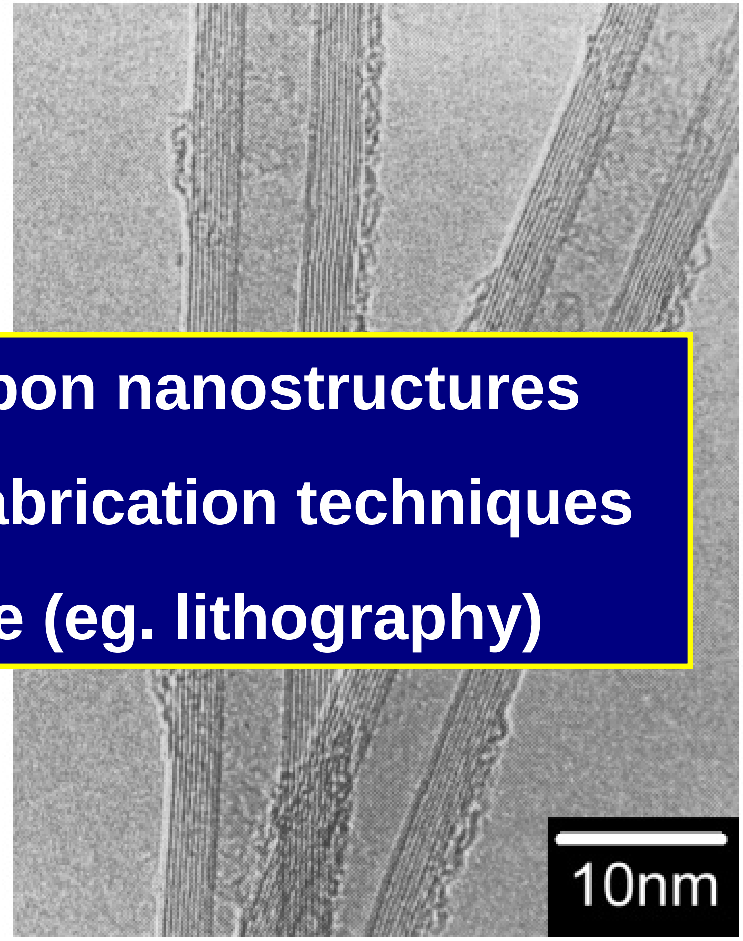
Novel Graphitic Carbon Materials





Single wall nanotubes by CVD
Dai, JPCB 103, 11246 (1999)



Multiwall nanotubes by arc discharge
Harris, Carbon Nanotubes and rel struc.

gmuir 11,
62 (1995)

Synthesis of carbon nanostructures does not require fabrication techniques at the nanoscale (eg. lithography)

Why are carbon nanotubes technologically important?

- With walls parallel to the filament axis, several favourable properties are inherited from intra-plane graphite:
  - High electrical conductivity
  - High thermal conductivity
  - High mechanical strength and modulus
  - Very few dangling bonds or edges – inert
  - Covalently bonded – no electromigration
  - 1-D single wall tubes can be metallic or semi conducting and exhibit quantum effects.

Historical Background

- Attributed mainly to Iijima [Nature **354**, 56 (1991)] who observed "microtubules of graphitic carbon" in the cathode deposit of arc discharge of graphite.

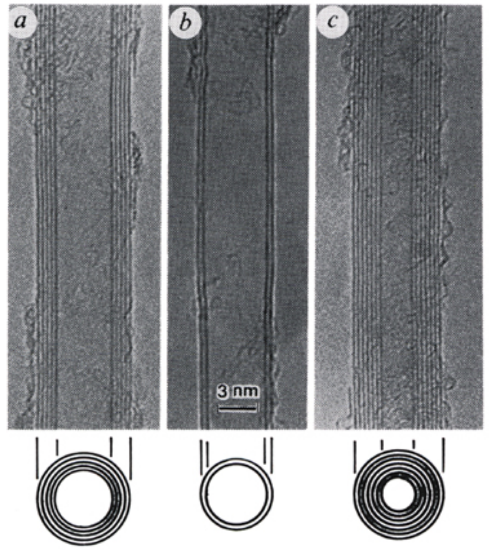
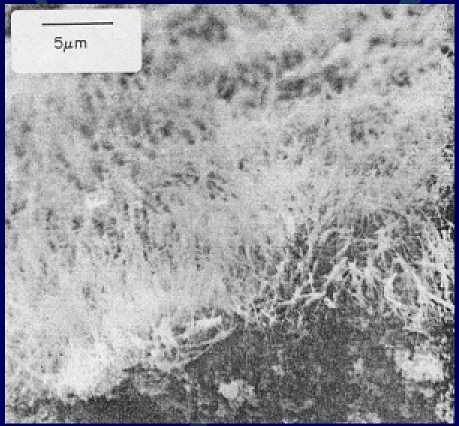
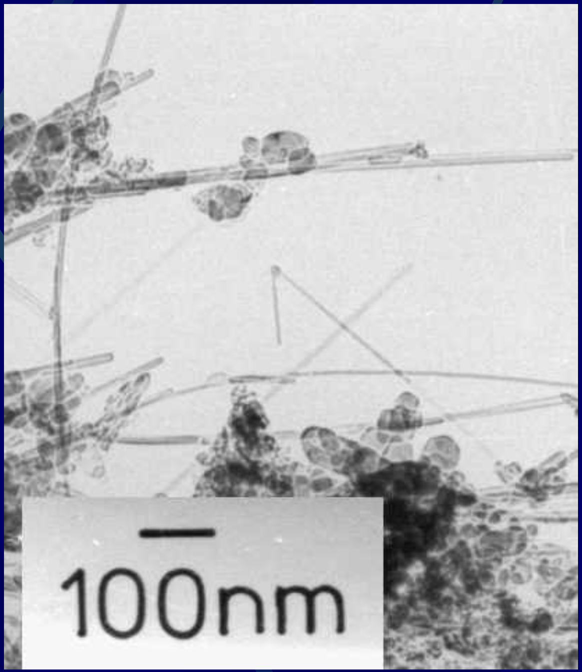


FIG. 1 Electron micrographs of microtubules of graphitic carbon. Parallel dark lines correspond to the (002) lattice images of graphite. A cross-section of each tubule is illustrated. *a*, Tube consisting of five graphitic sheets, diameter 6.7 nm. *b*, Two-sheet tube, diameter 5.5 nm. *c*, Seven-sheet tube, diameter 6.5 nm, which has the smallest hollow diameter (2.2 nm).

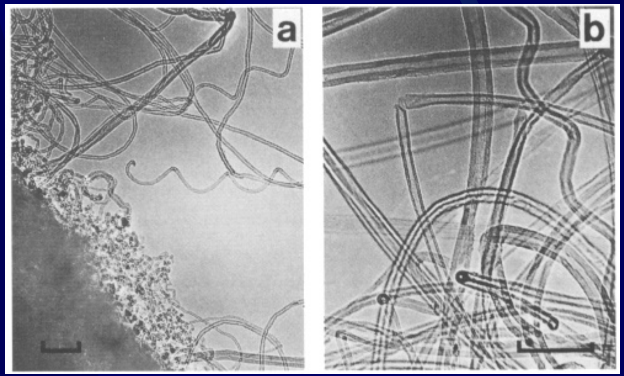
Pre-1991 evidence?

- Eg. Filaments from arc discharge in He by Wiles et al, *Carbon* **16,** 341 (1978).



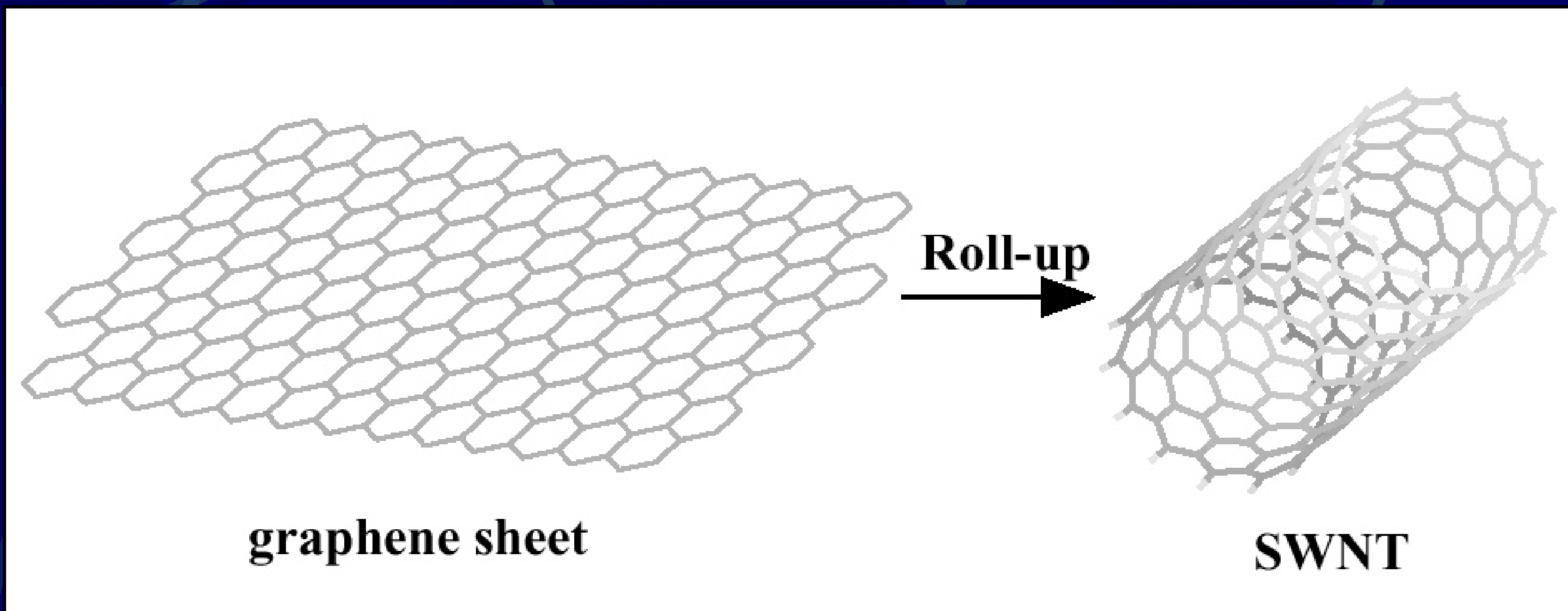


- Eg. Catalytic growth of carbon filaments by Baker and Harris (1960's-80's)



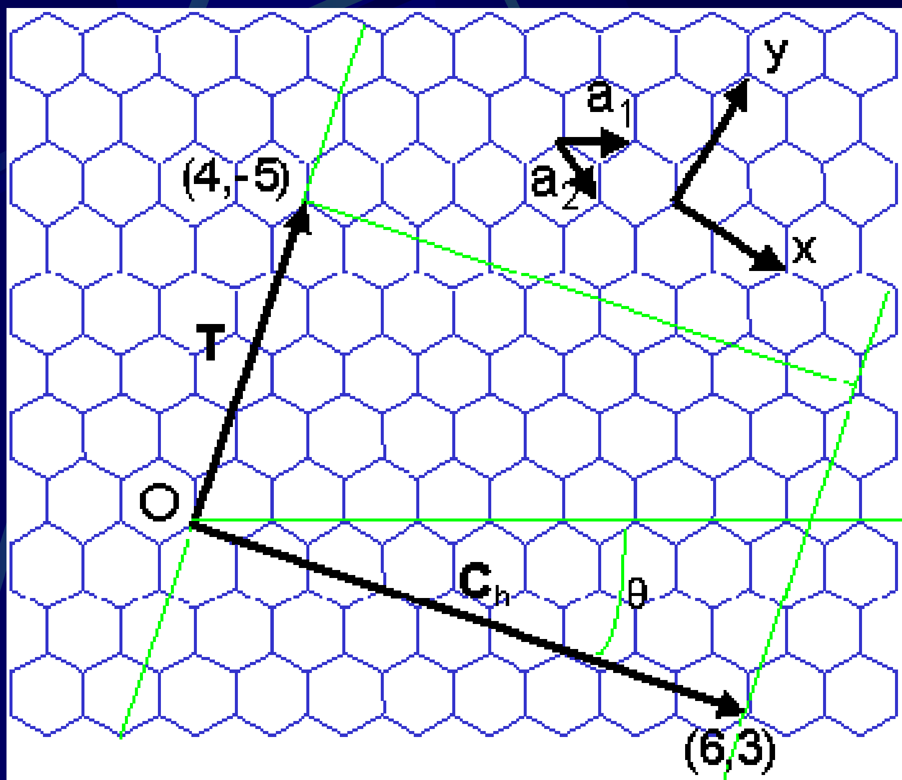
Electronic Structure of SWNT

- Single wall nanotubes can be semiconducting!



- It all depends on the angle of rolling and diameter of the nanotube.

Definition of Chiral Vectors



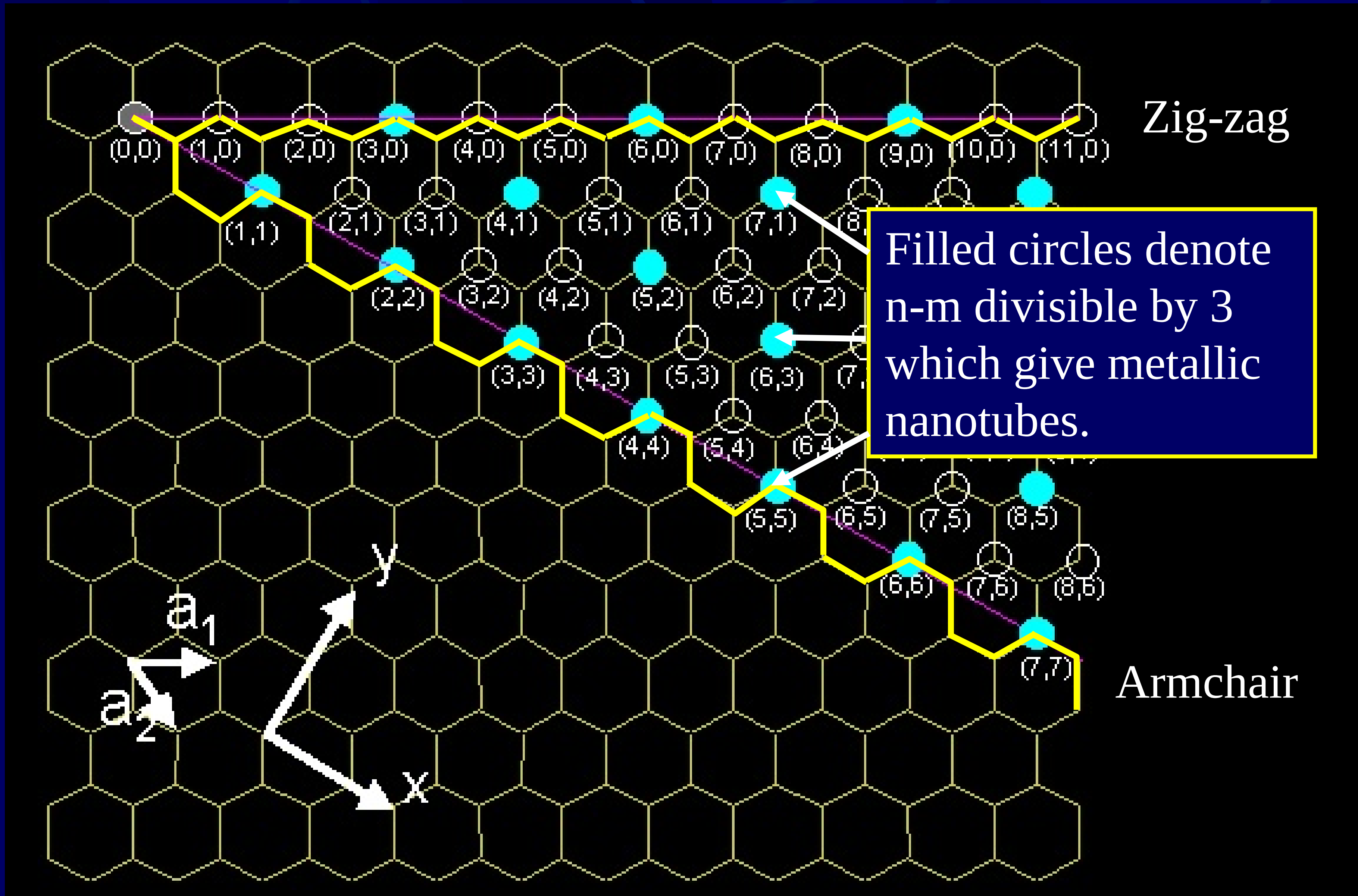
$C_h = n\mathbf{a}_1 + m\mathbf{a}_2$

$|\mathbf{a_1}| = |\mathbf{a_2}| = \sqrt{3}a_{cc} = a$
(a is unit length)

Length of C_h =
$\sqrt{3}a_{cc}\ (n^2 + mn + m^2)^{0.5}$
Hence, $d_t = C_h/\pi$

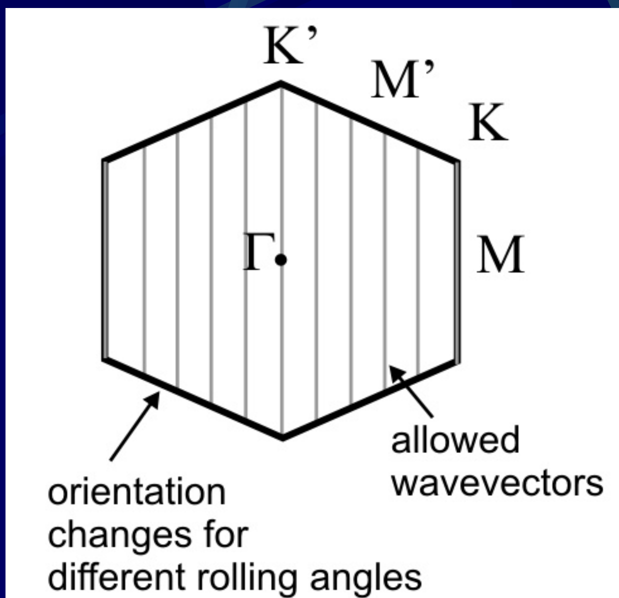
Transational Vector T=
$[(2m+n)\mathbf{a_1} - (2n+m)\mathbf{a_2}]/d$

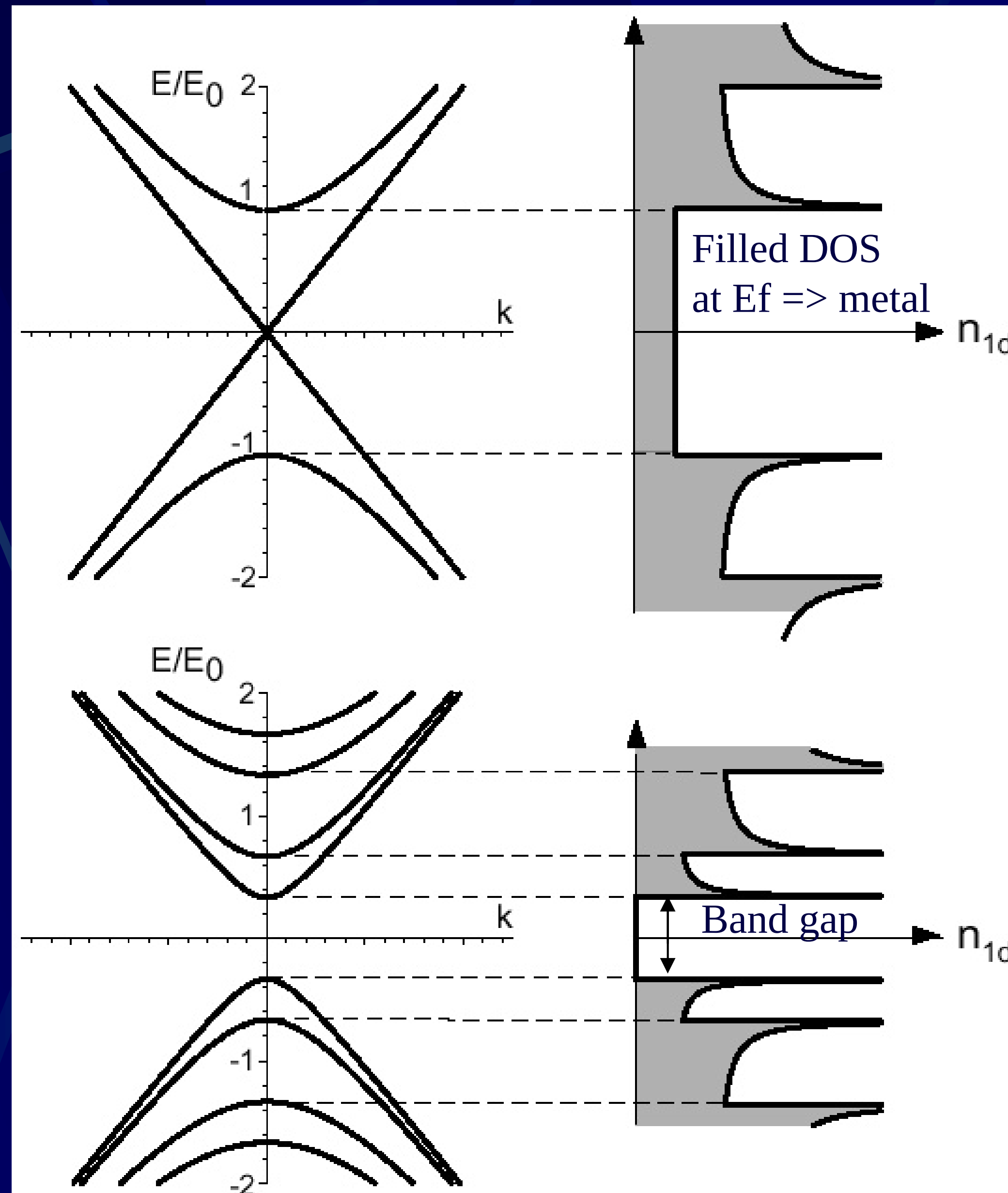
Chiral Angle θ =
$\tan^{-1} [\sqrt{3}m/(m+2n)]$



Zig-zag
Armchair
Filled circles denote n-m divisible by 3 which give metallic nanotubes.
(0,0) (1,0) (2,0) (3,0) (4,0) (5,0) (6,0) (7,0) (8,0) (9,0) (10,0) (11,0)
(1,1) (2,1) (3,1) (4,1) (5,1) (6,1) (7,1)
(2,2) (3,2) (4,2) (5,2) (6,2) (7,2)
(3,3) (4,3) (5,3) (6,3)
(4,4) (5,4)
(5,5) (6,5) (7,5) (8,5)
(6,6) (7,6) (8,6)
(7,7)
a_1
a_2
y
x

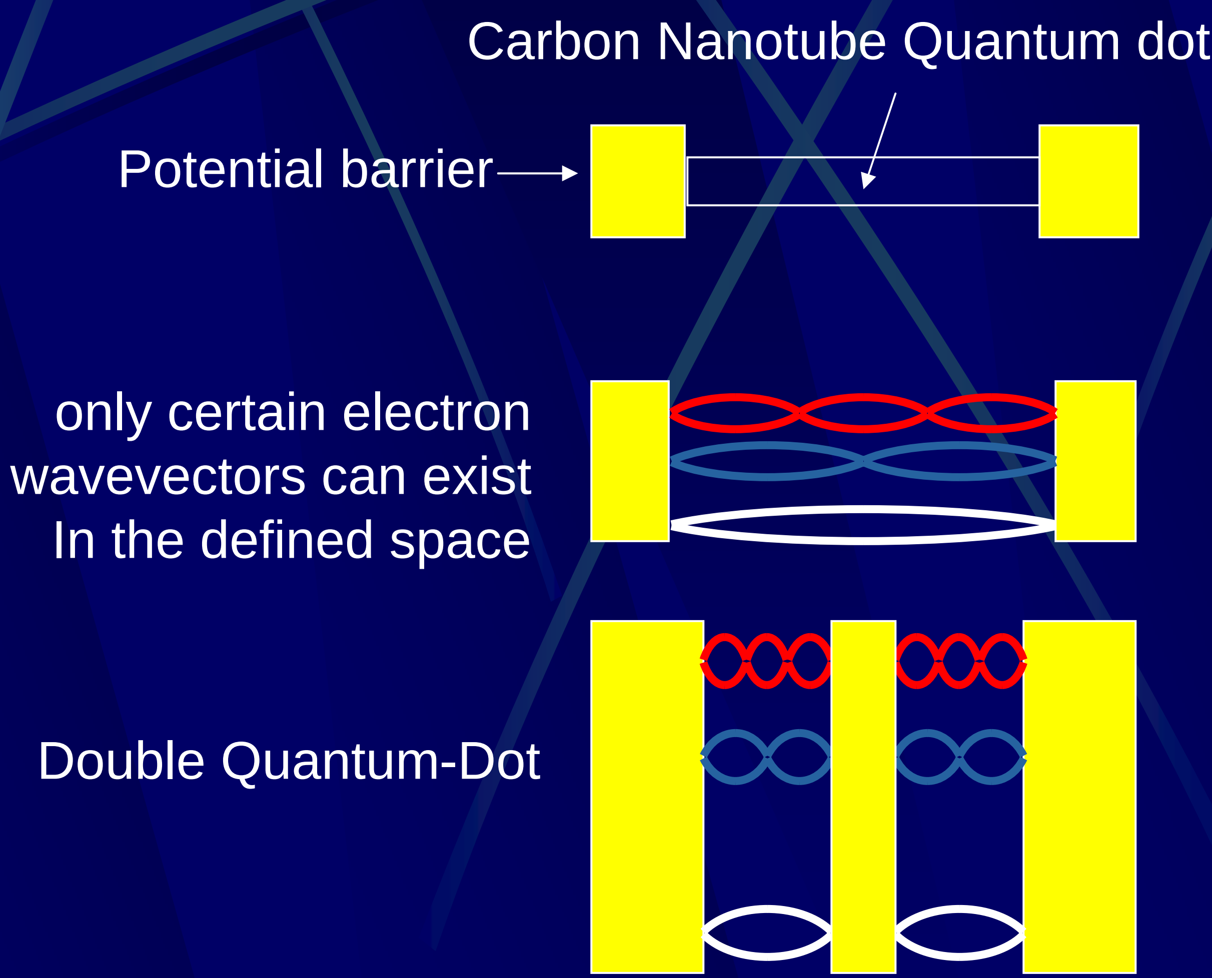
Metallic





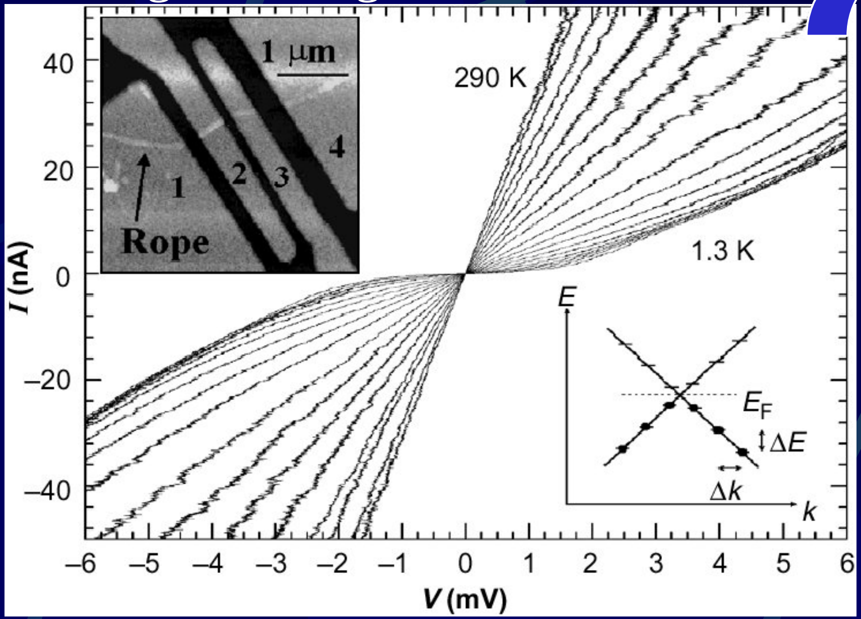
Semiconducting

Quantum confinement in nanotubes

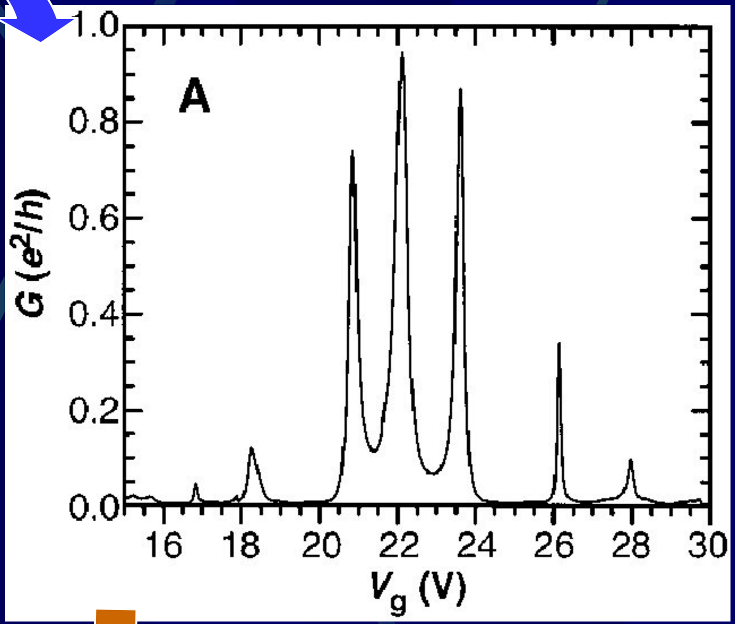


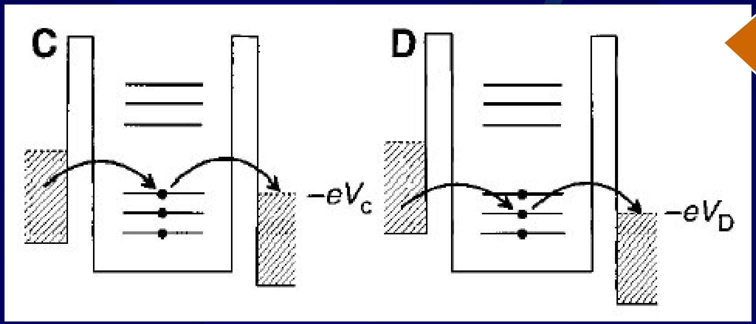
Single Electron Transport

At no gate voltage



Conductance vs gate voltage

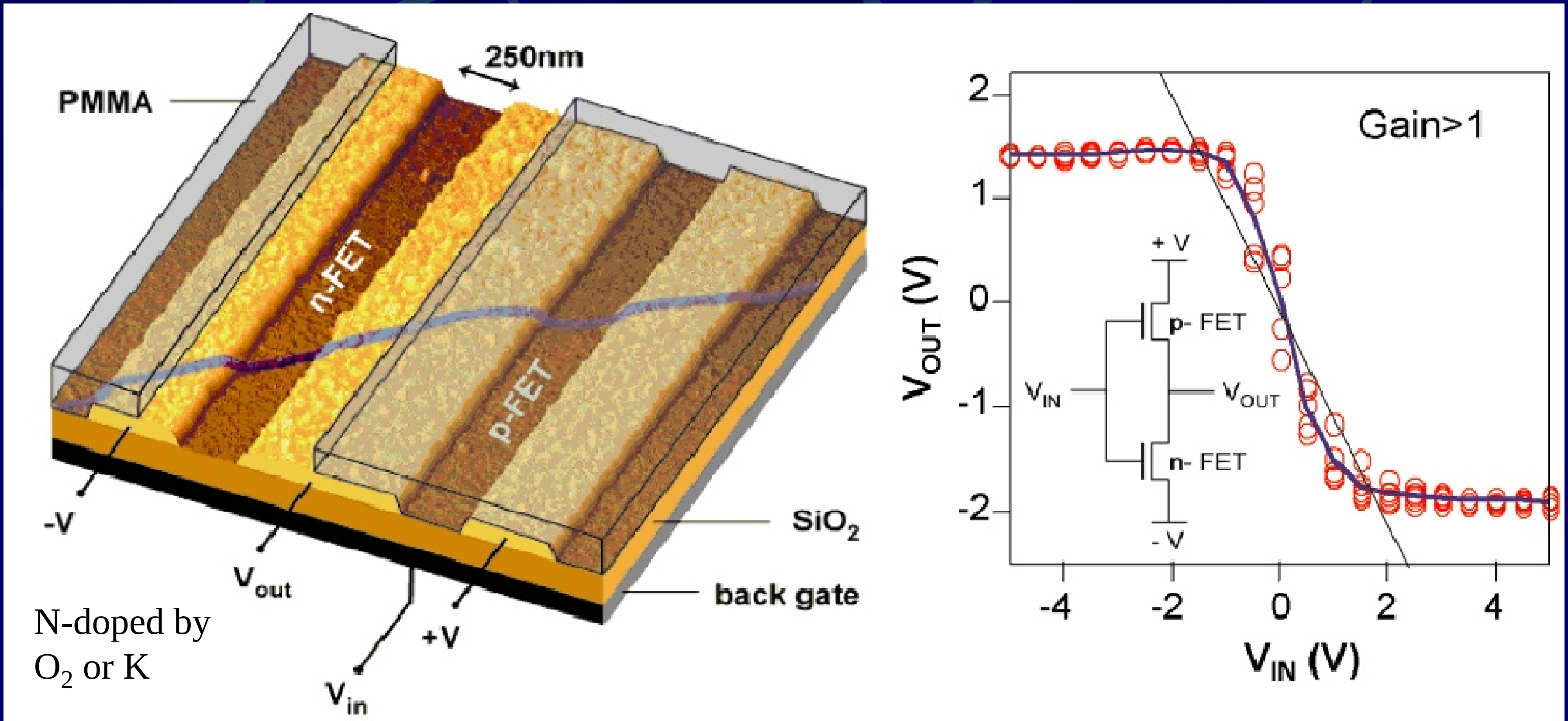




Single electron transport from discrete states are being observed.

Bockrath, Science **275**, 1922 (1997)

Single CNT Inverter by IBM

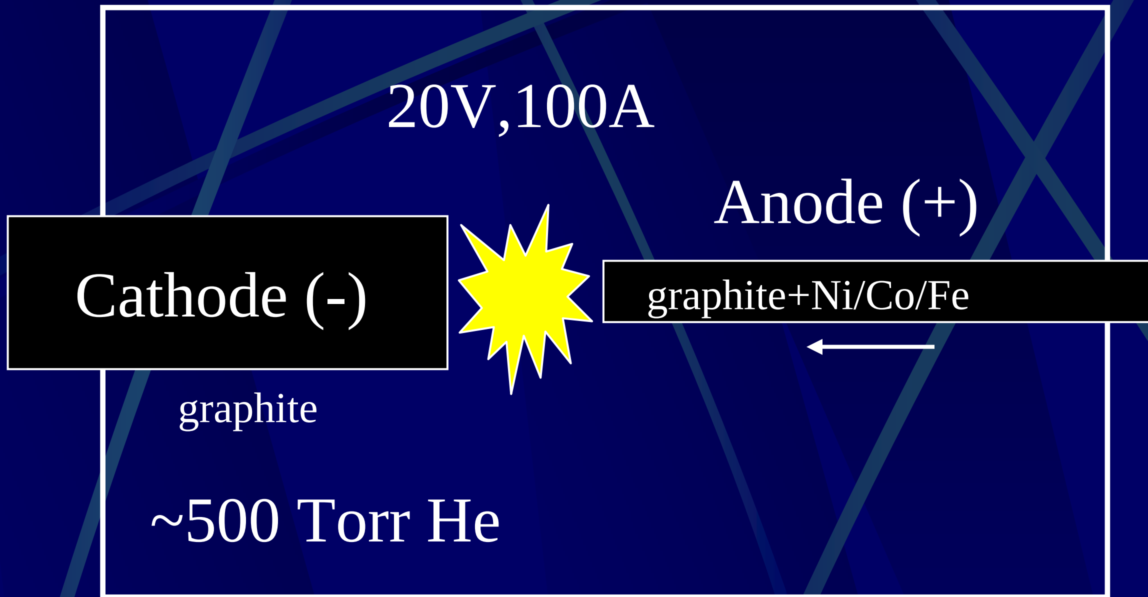


Derycke et al, Nano Lett 1, 453 (2001)

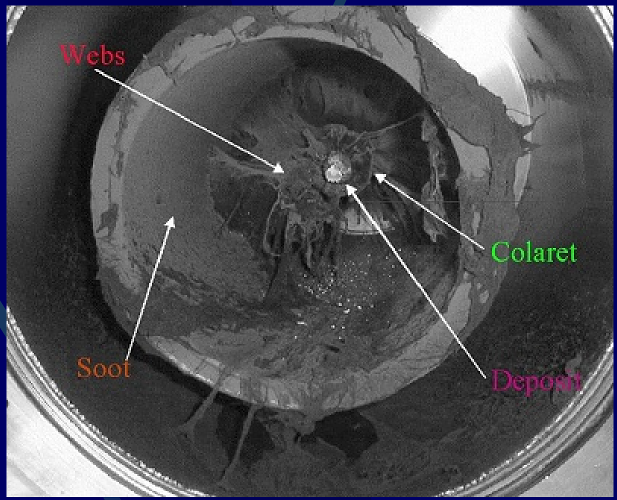
Growth of Carbon Nanotubes

- Electric arc discharge between graphite electrodes
- Laser ablation
- Catalytic chemical vapour deposition (CVD)

Electric arc discharge



cathode view

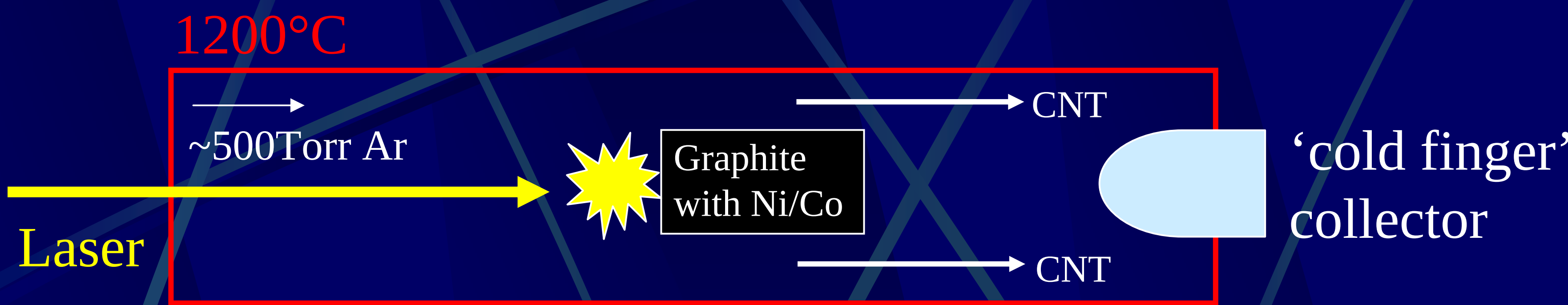


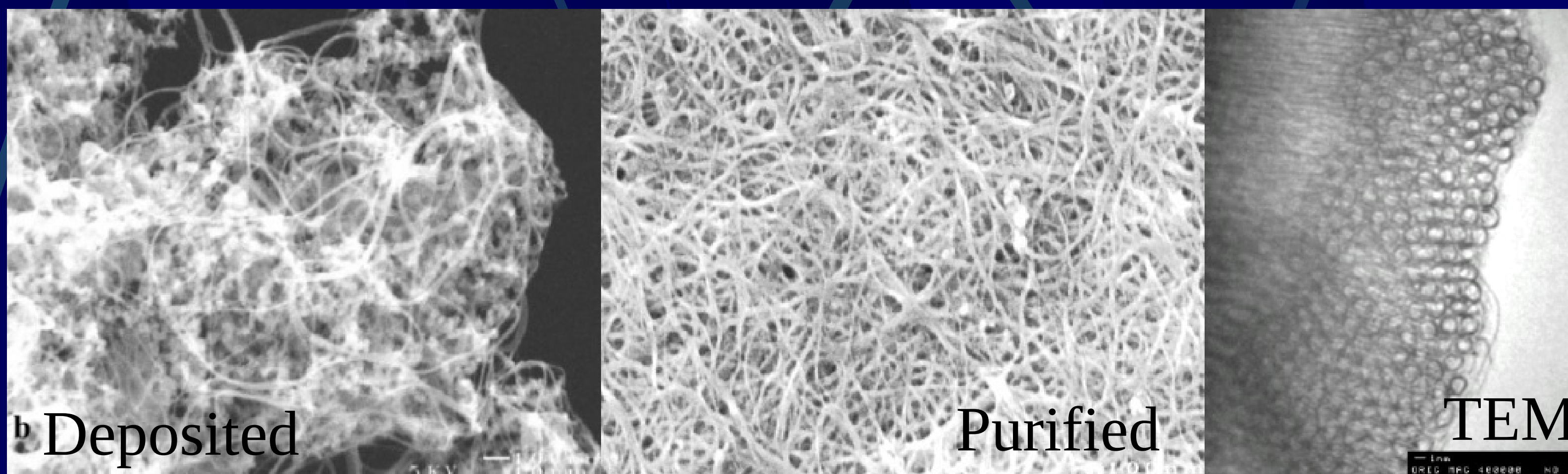
Bernier et al

Advantages: cheap equipment, fast production, produces both multiwall and single wall CNTs (add Ni/Co/Fe to anode for SWNT), very straight and highly crystalline nanotubes

Disadvantage: needs purification

Laser Ablation





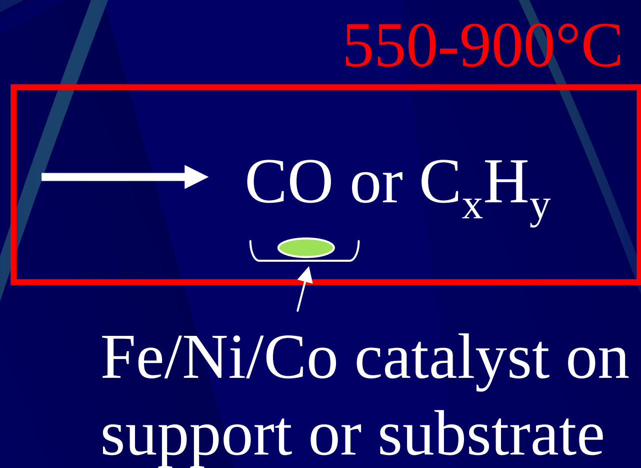
Dai, Appl. Phys. A 67, 29 (1998)

Advantages: fast production, higher purity than arc discharge, very long nanotubes

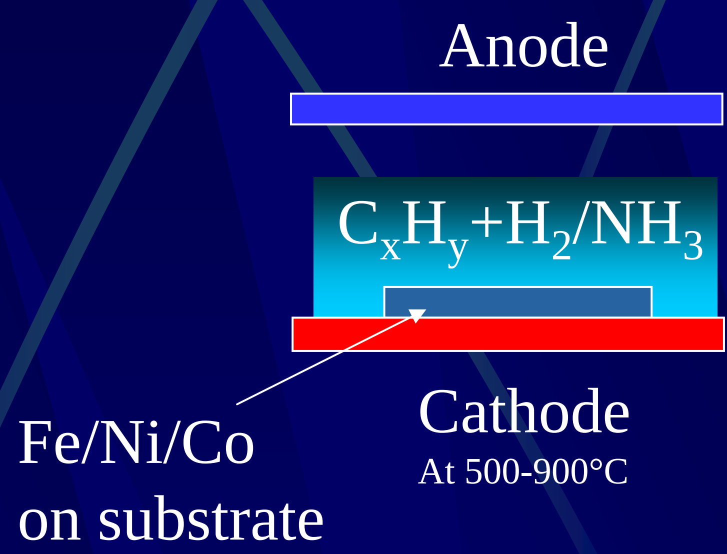
Disadvantages: still needs purification, expensive

Catalytic Chemical Vapour Deposition

Thermal CVD



Plasma CVD



Advantages: no purification needed, direct on substrate growth vertical floating technique can run continuously

Disadvantages: expensive compared with arc

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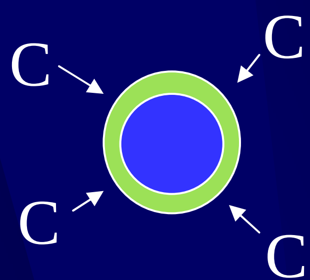
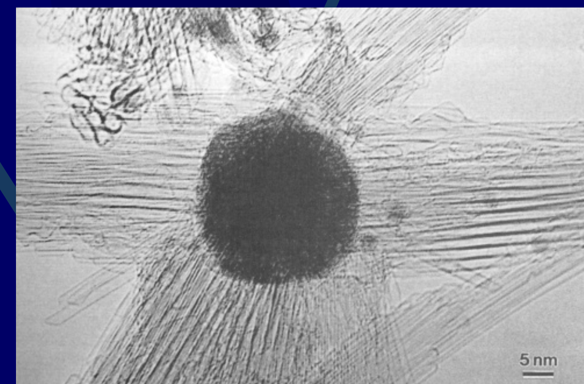
General formation mechanisms

- Arc discharge/laser ablation is a high temp but short time reaction



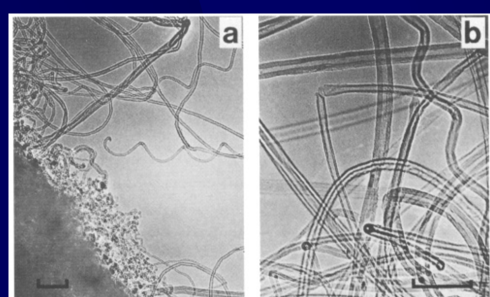
Dissolving C
in catalyst at 3000°C

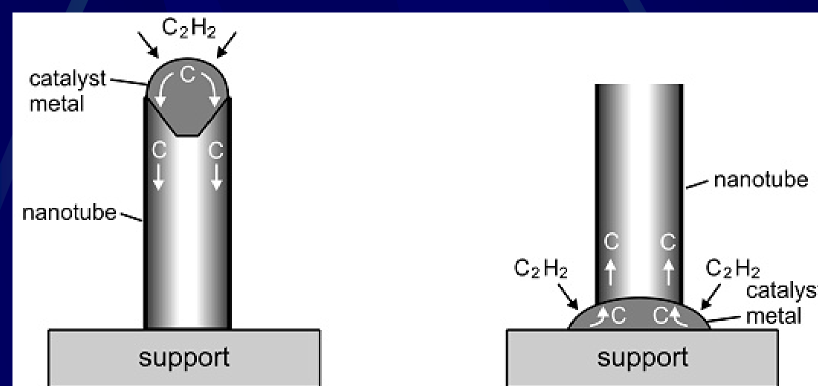
Extrusion of CNT by VLS
as temperature is quenched



Gavillet, PRL 87, 275504 (2001)

- Catalytic CVD is a low temp but long time reaction



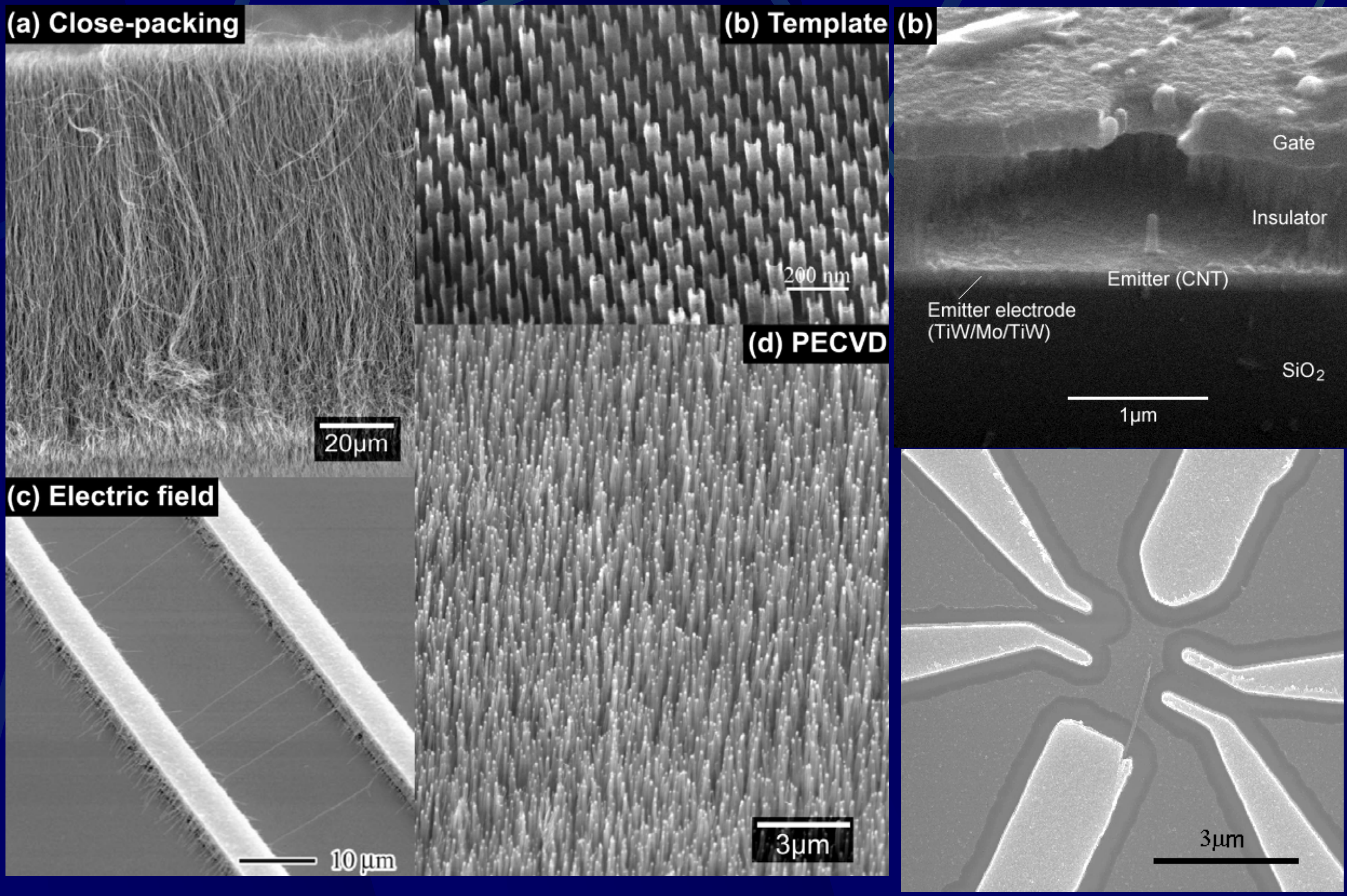


Baker, Carbon 27, 315 (1989)

Electrical/Electronic Applications

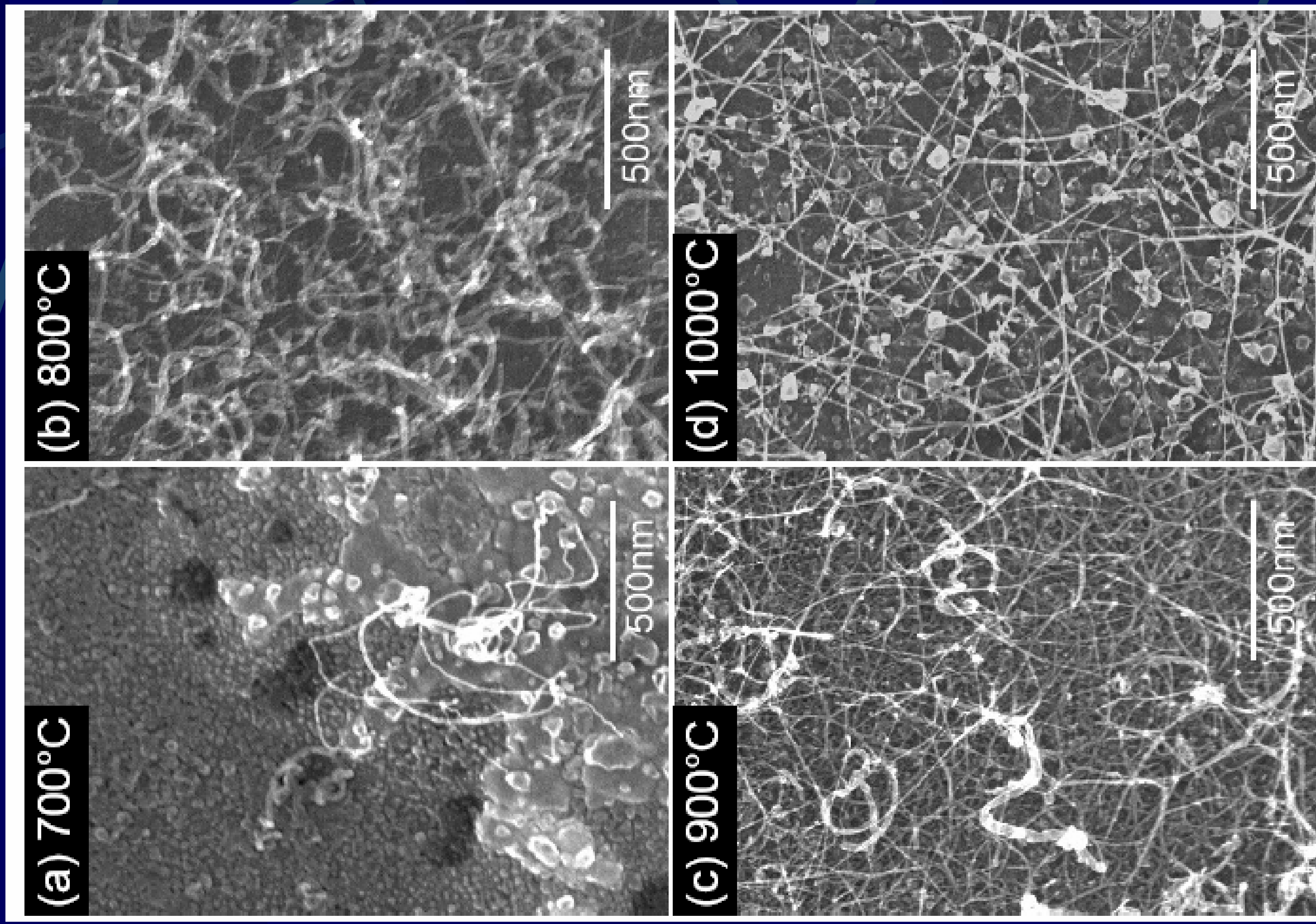
- Transistors
- Field emission devices
- Interconnects
- Solar cells
- Quantum effect devices

Examples of Aligned Nanotube Growth

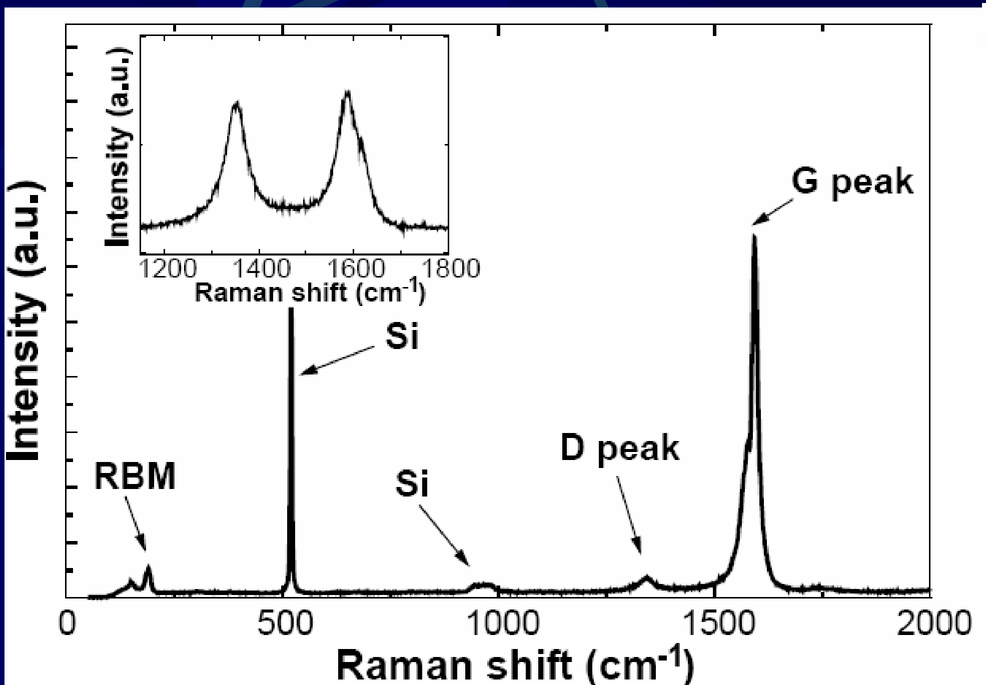


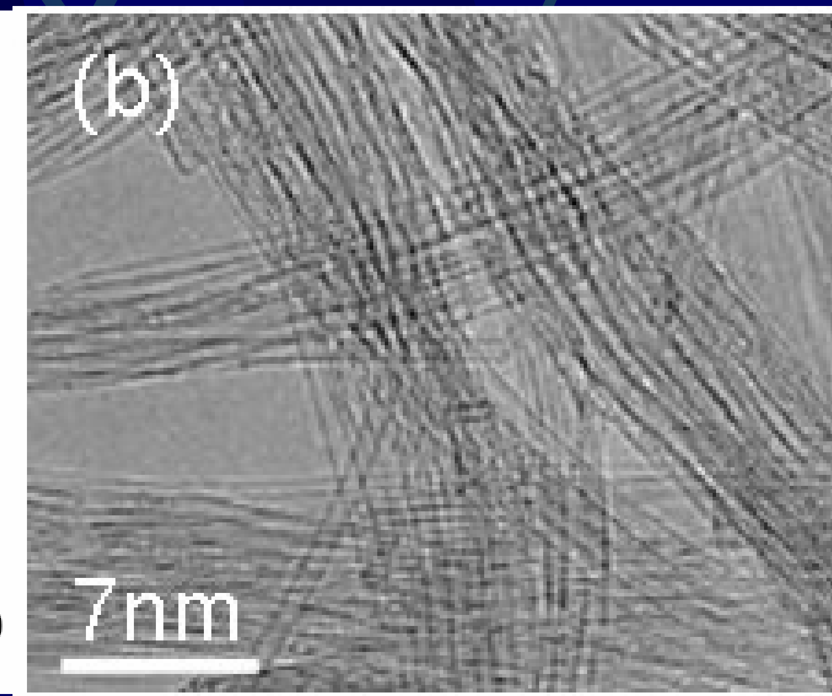
SWNTs Growth

MWNTs are obtained below 900°C. Growth time = 5s



Confirmation of SWNTs

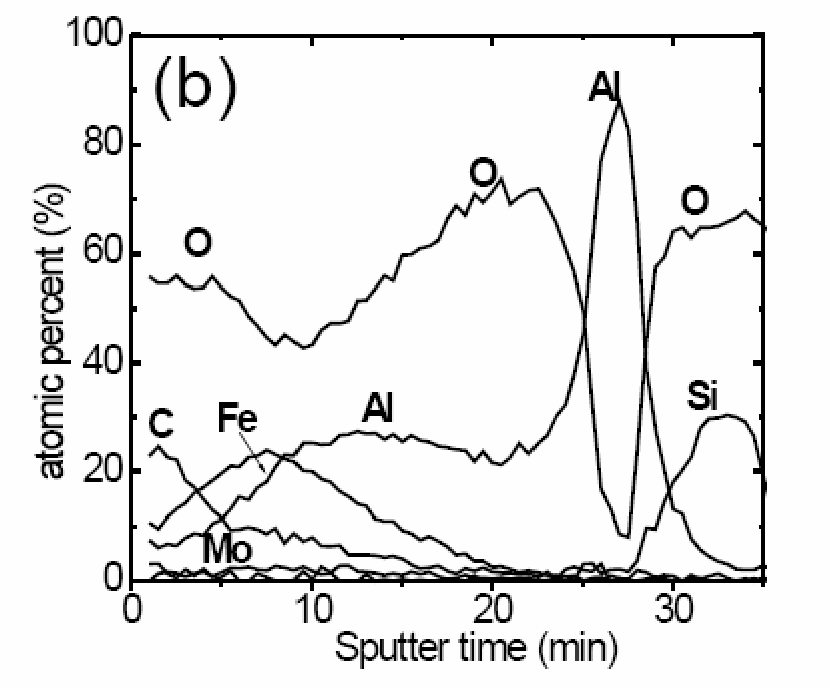




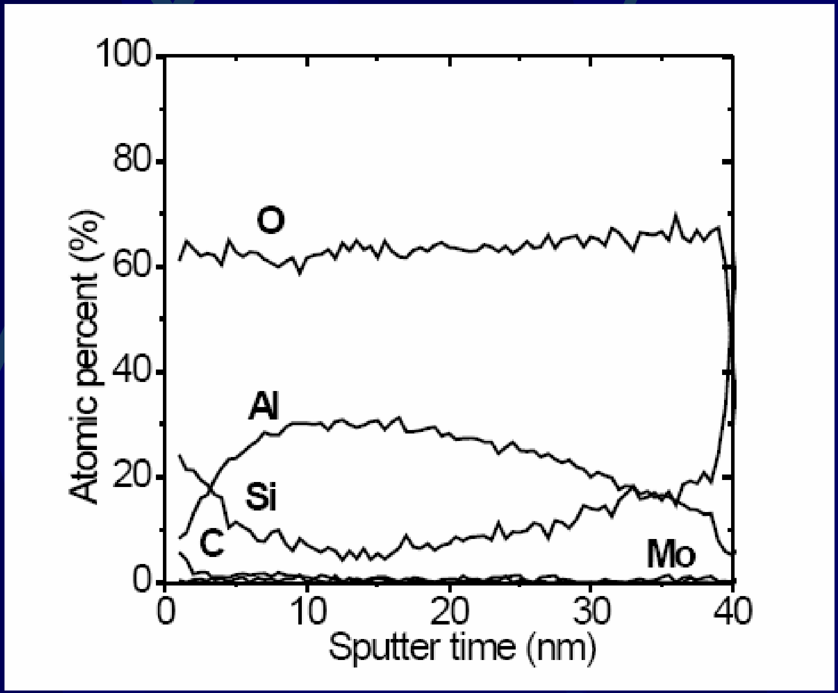
Dominant diameter obtained with both Raman & TEM is 1.2 – 1.3nm.

Auger Analysis of Catalyst

As-Deposited Fe/Mo/Al layer



After Annealing at 1000^oC



- The Al layer almost completely transforms to Al_xO_y after annealing

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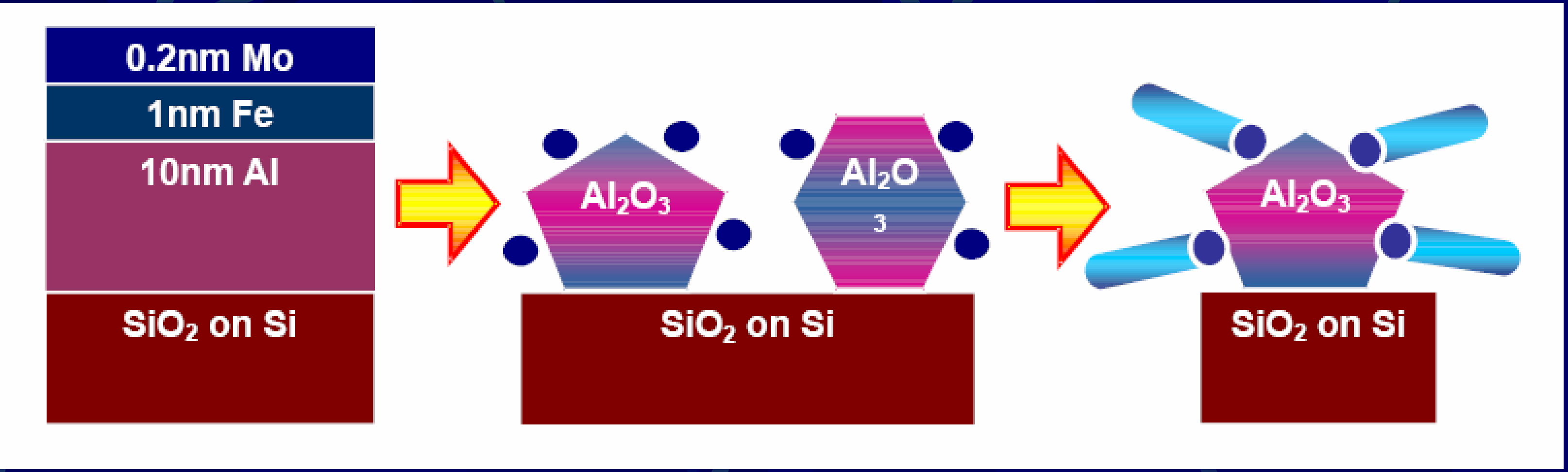
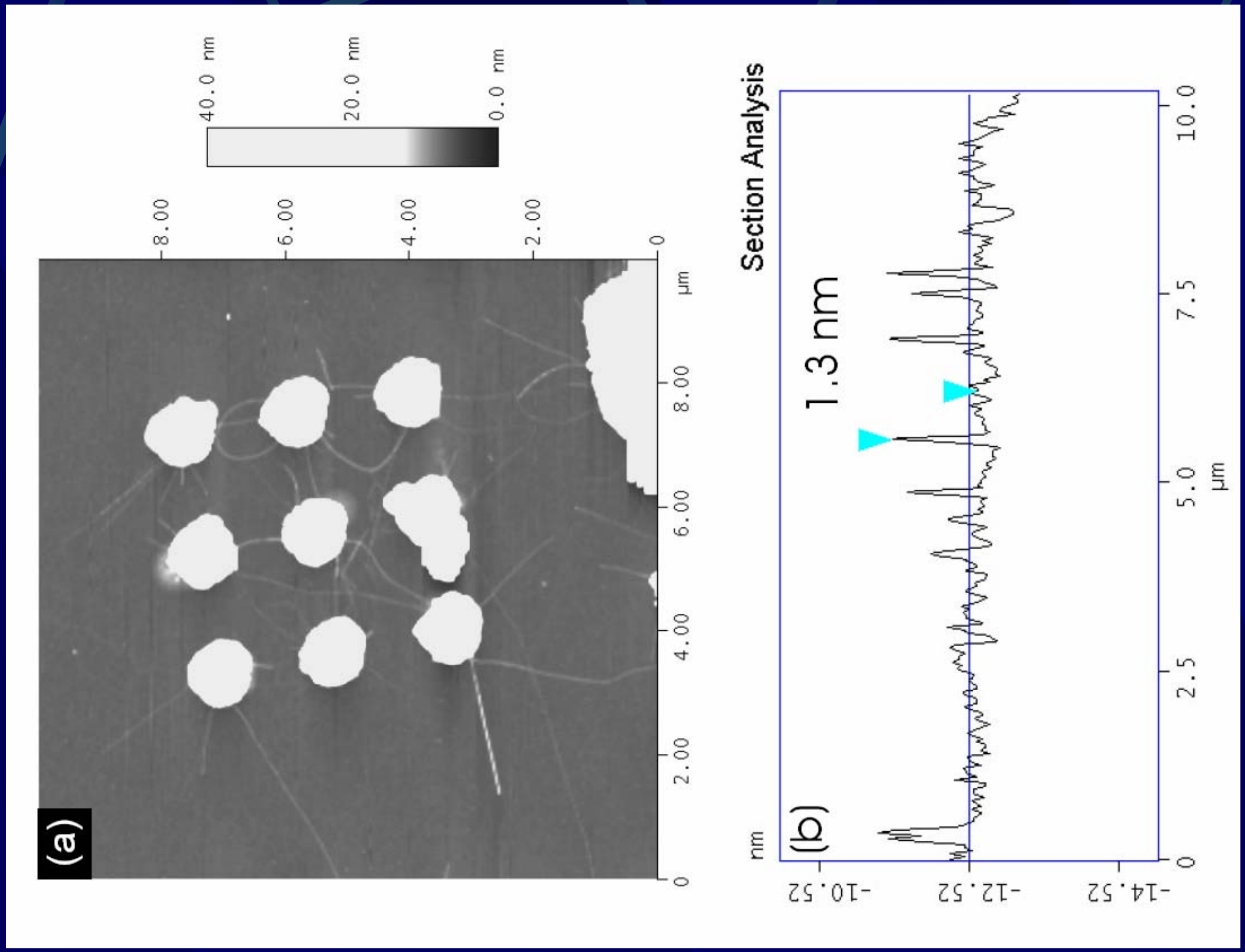
SWNT Formation Mechanism



- Mo acts as a growth facilitator
- Formation of Al_xO_y retards diffusion of Fe
- Formation of Fe nanoparticles favorable
- At low temps Al not completely oxidized so Fe diffuses to form larger aggregate catalyst

Patterned Growth of SWNTs



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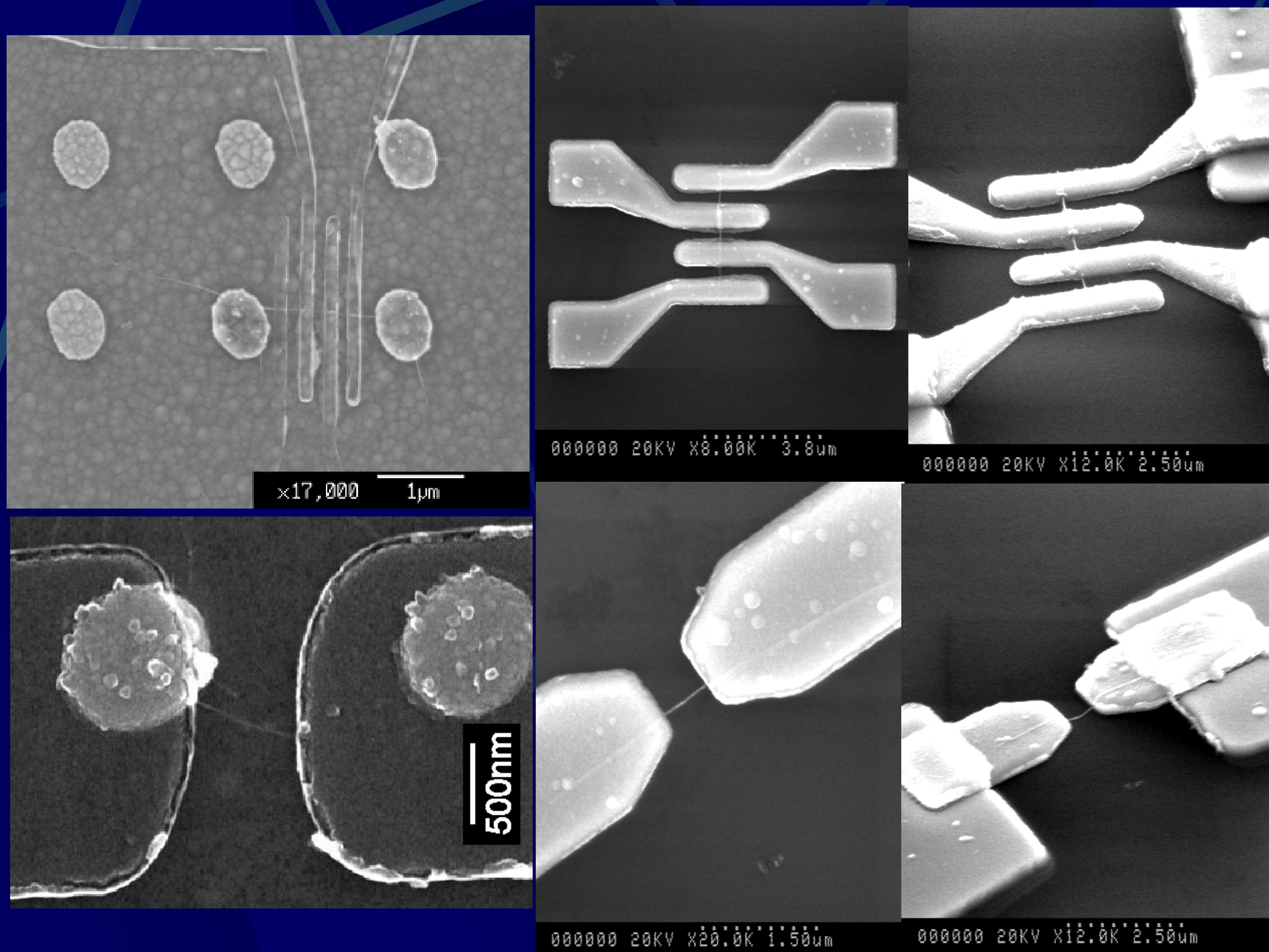
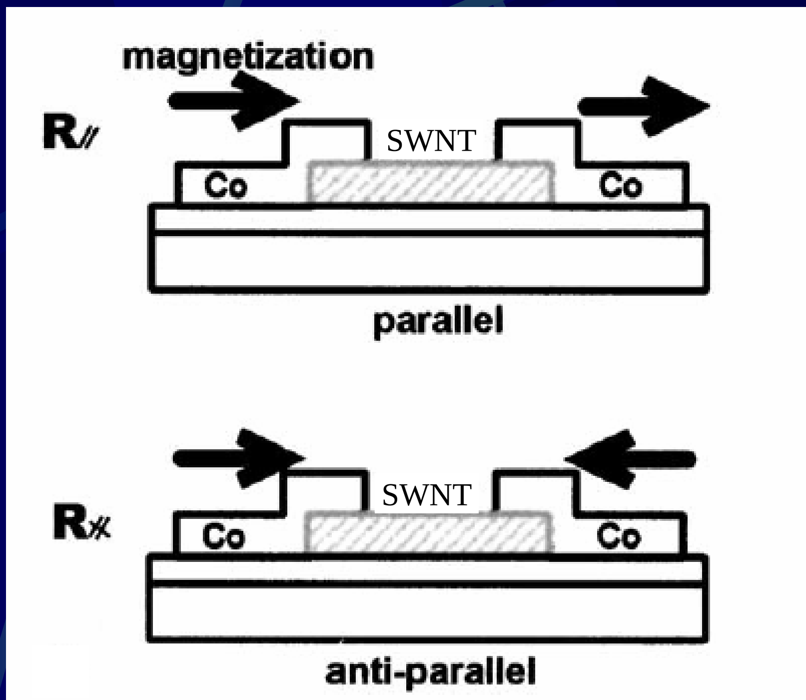
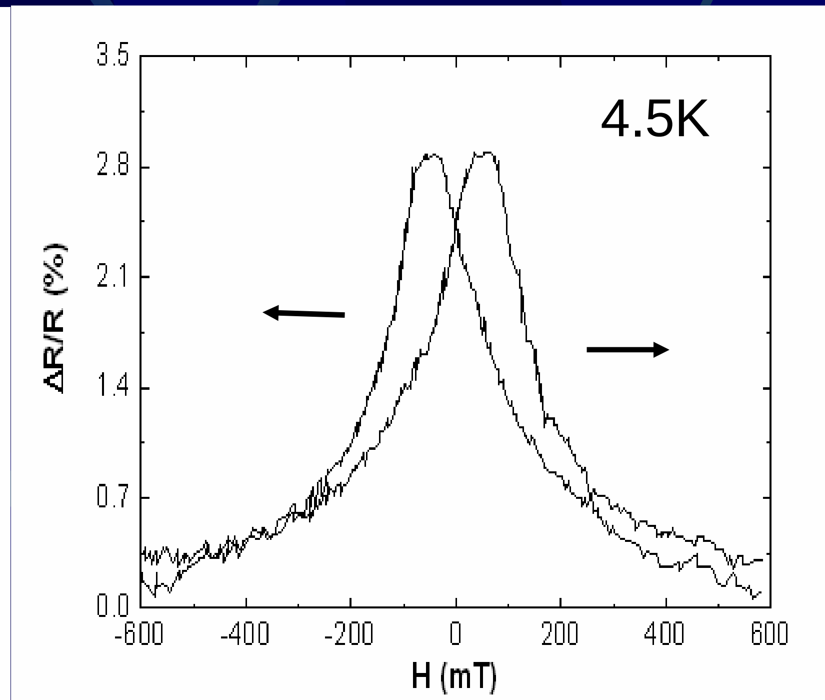
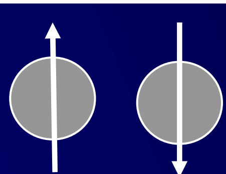
SWNT Devices



Spin transport in SWNTs







- Electrons can have spin up or down
- Spins in FMs can be aligned with magnetic fields

Useful for next generation of quantum computers

Conclusions

- High quality SWNTs can be grown on substrates.
- Devices with multiple electrodes can be fabricated
- Quantum effects can be exploited.

PECVD Grown Vertically Aligned Multi walled carbon nanotubes/nanofibers

- Growth and Field Emission Applications

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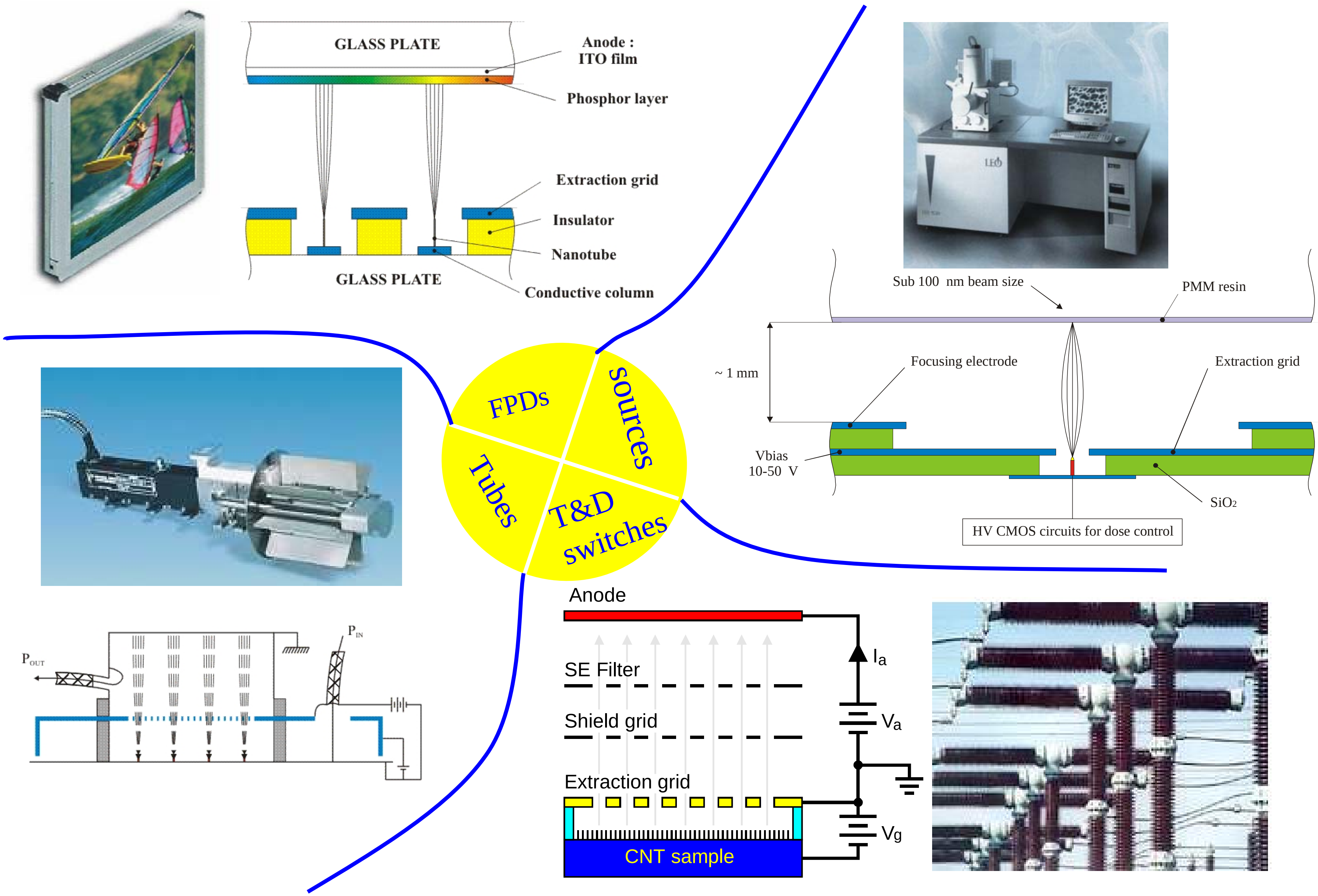
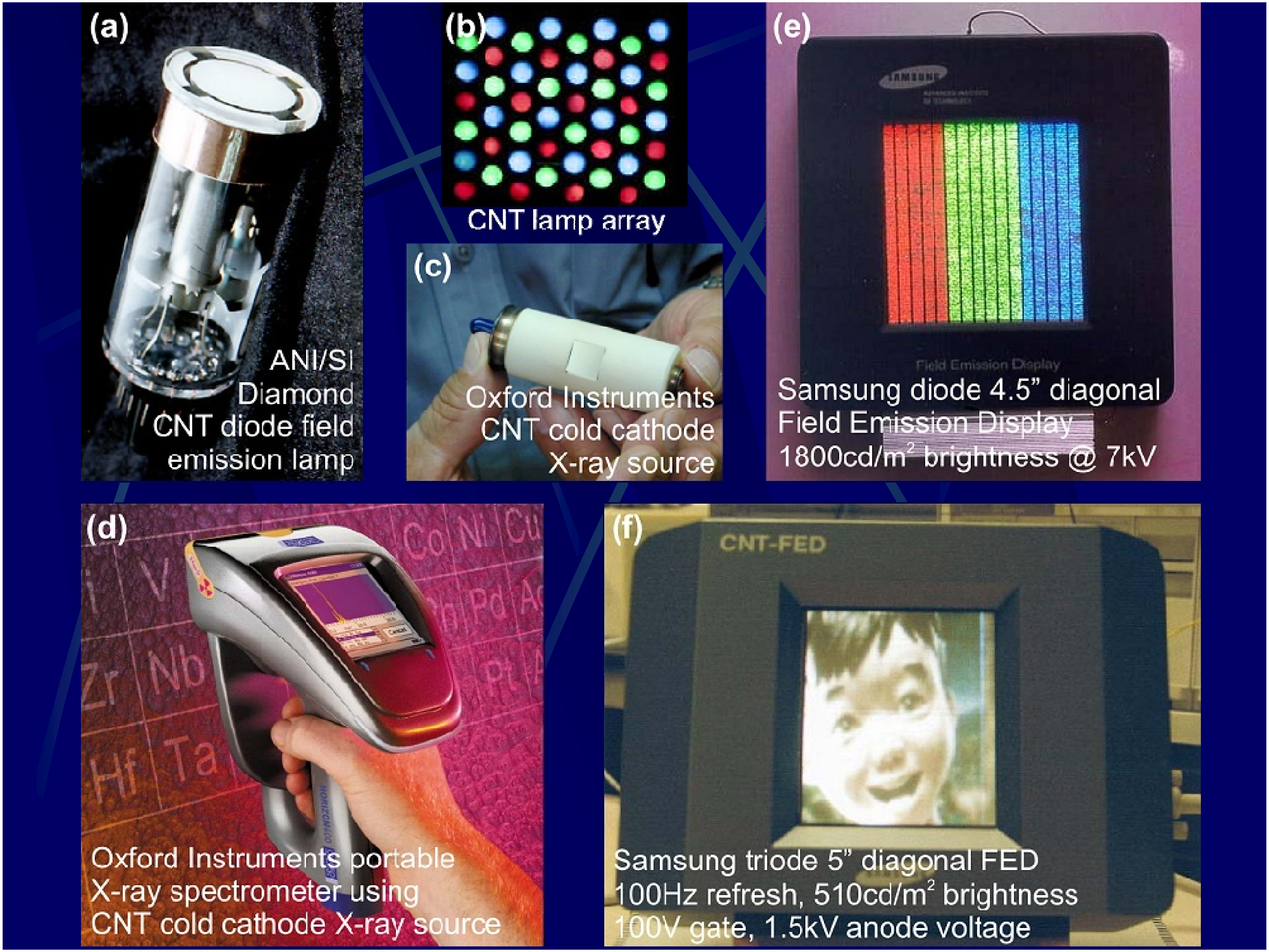
Field Emission Applications We are Investigating

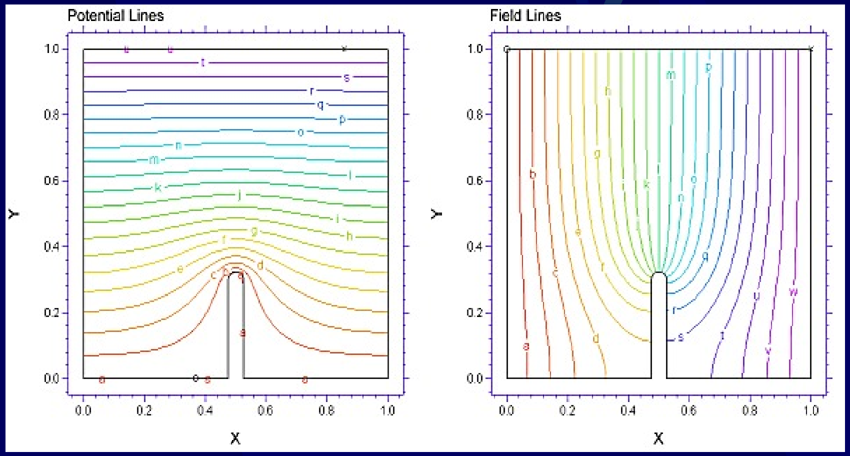


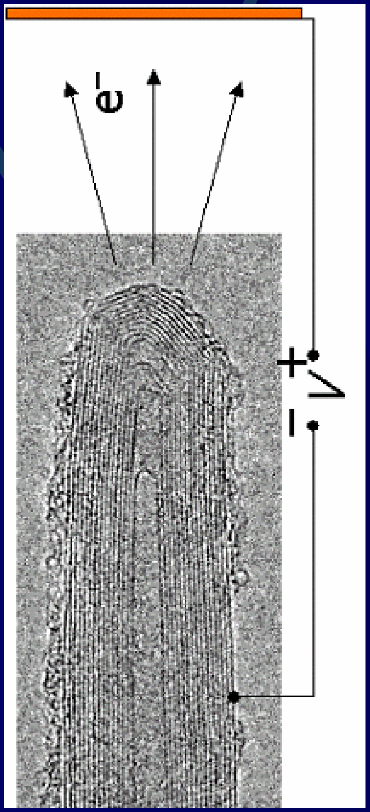

(a)
ANI/SI
Diamond
CNT diode field
emission lamp
(b)
CNT lamp array
(c)
Oxford Instruments
CNT cold cathode
X-ray source
(e)
Samsung diode 4.5” diagonal
Field Emission Display
1800cd/m² brightness @ 7kV
(d)
Oxford Instruments portable
X-ray spectrometer using
CNT cold cathode X-ray source
(f)
CNT-FED
Samsung triode 5” diagonal FED
100Hz refresh, 510cd/m² brightness
100V gate, 1.5kV anode voltage

Field Emission Applications

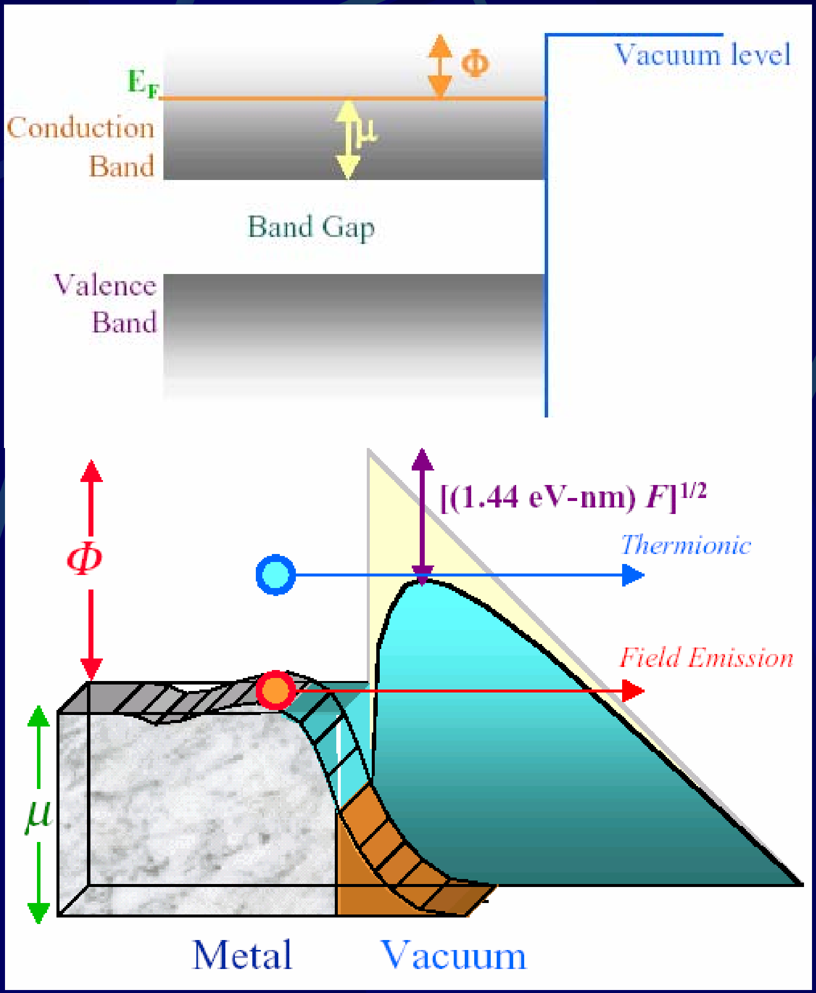
- CNT's are favourable as field emission electron sources because they have:
  - High aspect ratio
  - Small tip radius
  - High conductivity

    (NB. multiwall are non-semiconducting)





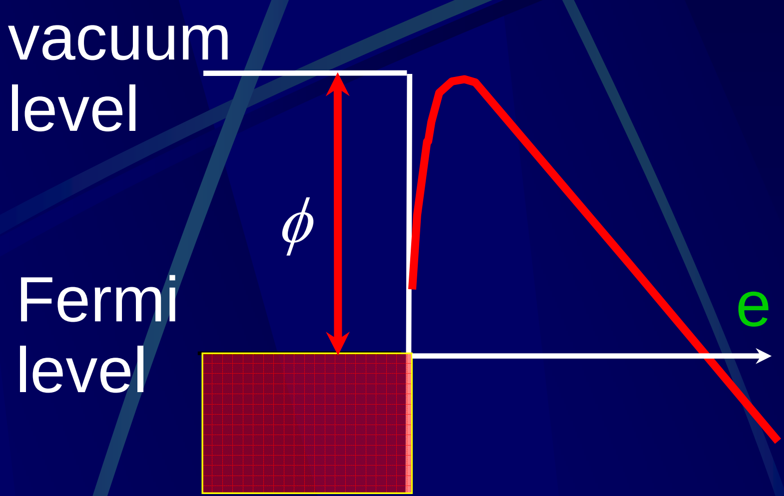
Electron Emission



- Large density of electrons exist in the conduction band
- Very small fraction contribute to emission current

- Most energetic electrons lie several eV below vacuum level
- Either temperature or voltage required for emission

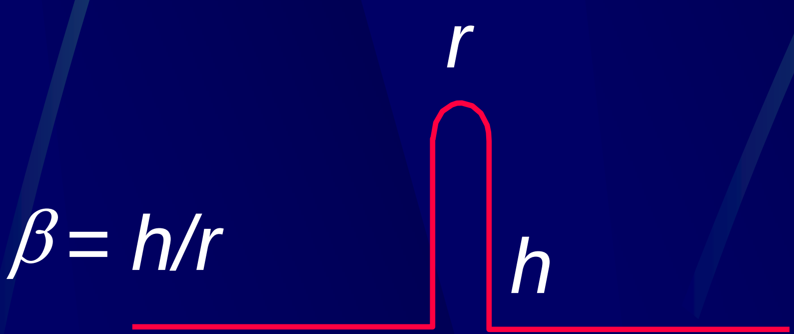
What is Field Emission?



- Electron tunnelling from solids under high local field (10^8 V/m)
- Fowler-Nordheim equation:

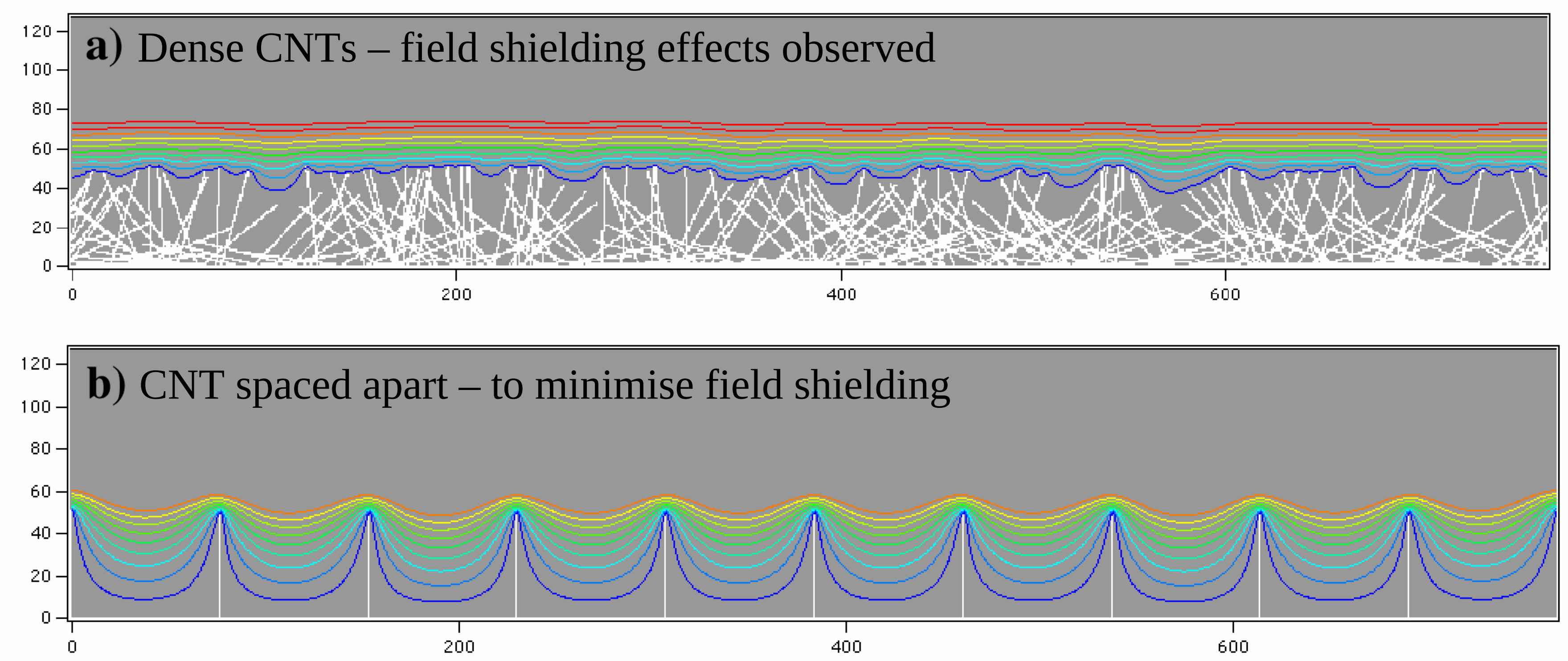
$$J = aF^2 \exp\left(-\frac{b\phi^{3/2}}{\beta F}\right)$$

- ϕ = barrier height
- Local field $F_L = \beta F$
- Fowler-Nordheim plot, $\ln(J/F^2) = c + d/F$
- Slope gives $\phi^{3/2}/\beta$ *not* ϕ

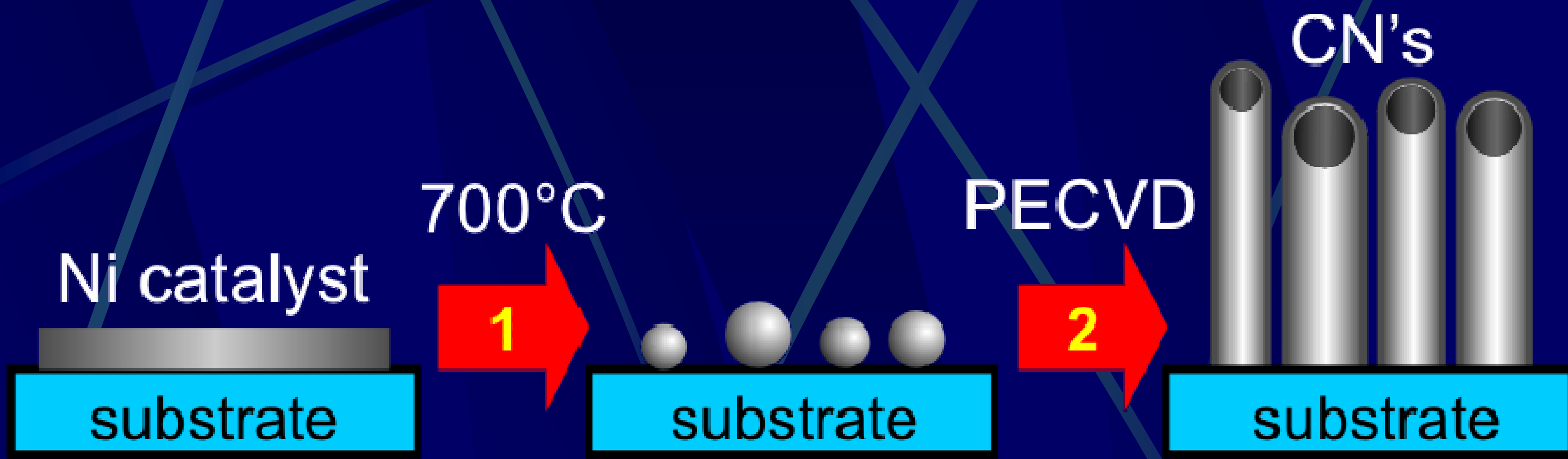


CNTs for Field Emission

- Dense forest of CNTs might not be as efficient as CNTs spaced apart due to electric field shielding effects.



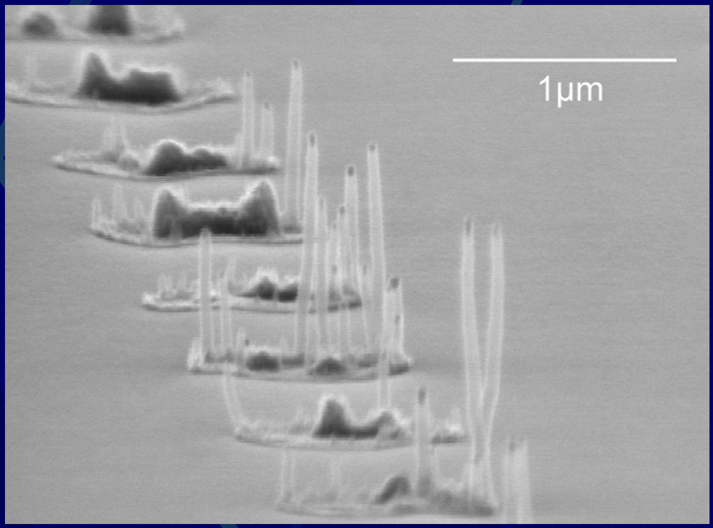
Plasma Enhanced-CVD of CNT's



- Step 1: At 700°C (growth temp), Ni catalyst agglomerates into catalyst clusters.
- Step 2: PECVD - C_2H_2 is the growth gas for CNTs, NH_3 is the etching gas for unwanted a-C.

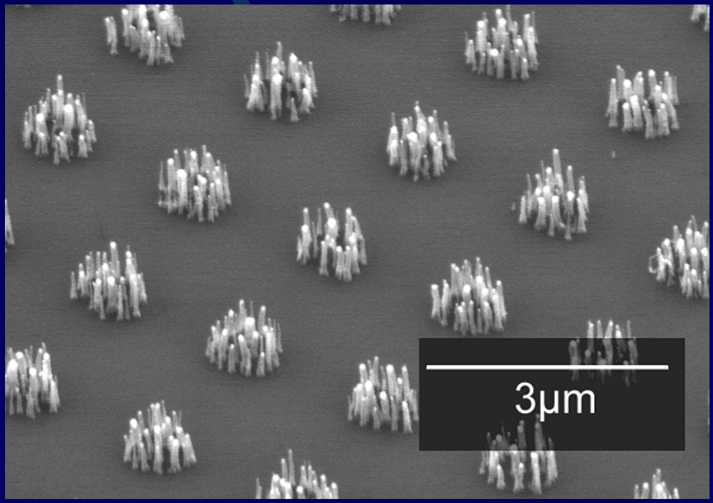
Diffusion Barrier for Si substrates

- Without diffusion barrier, Ni forms $NiSi_x$ at >300°C!



No barrier
(poor yield)

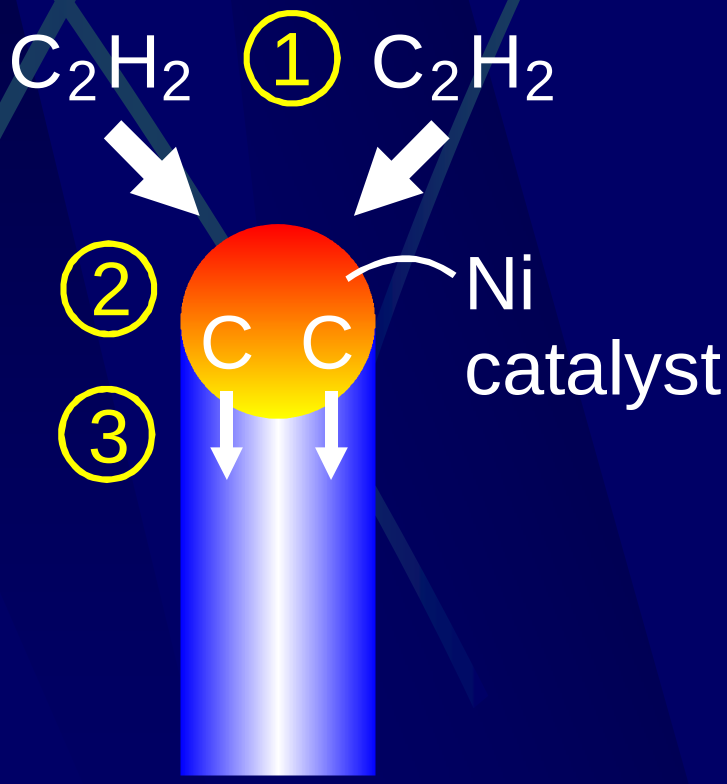
- Effective diffusion barriers – insulating SiO_2 or conductive TiN



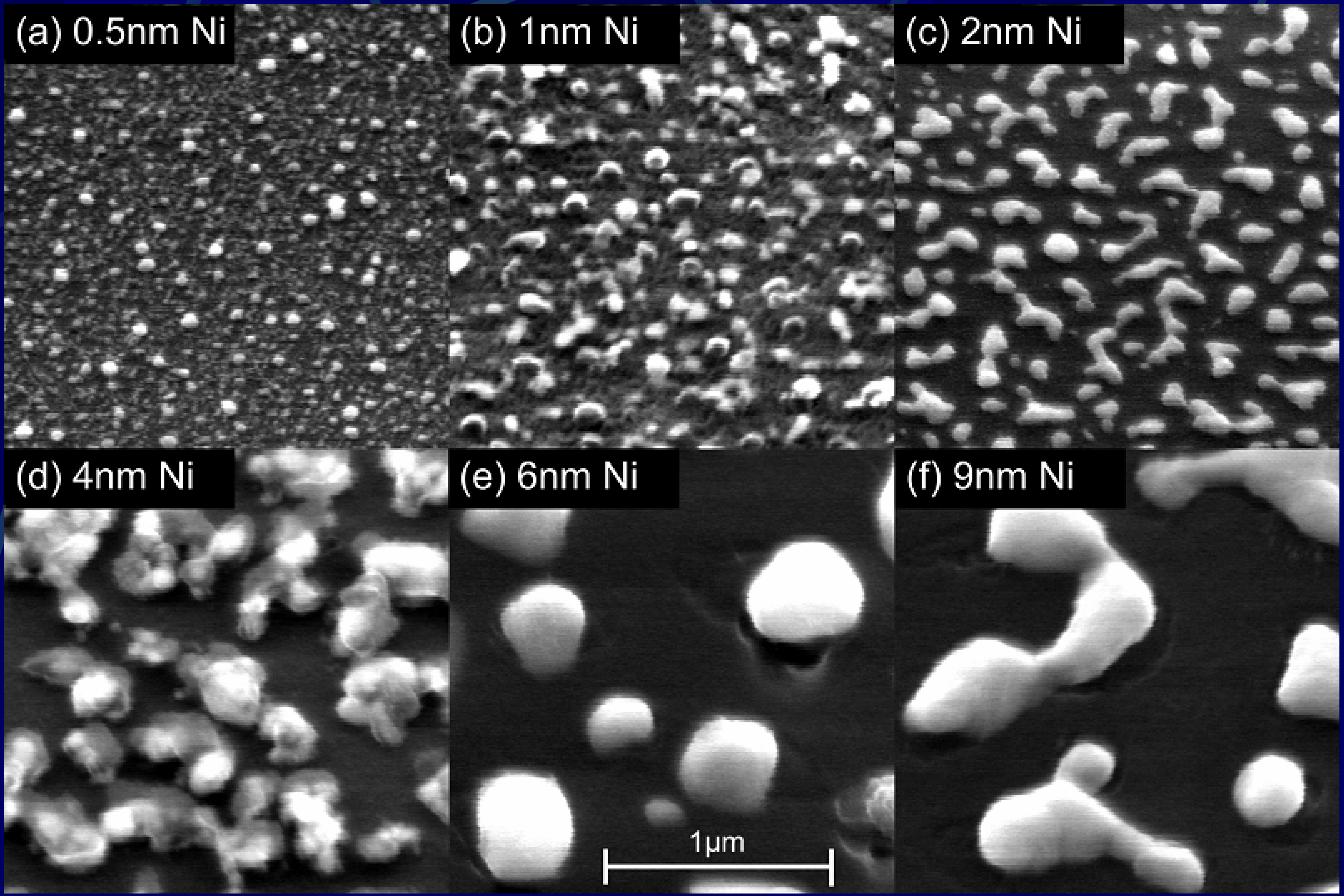
With barrier
(100% yield)

CNT VLS Growth Mechanism

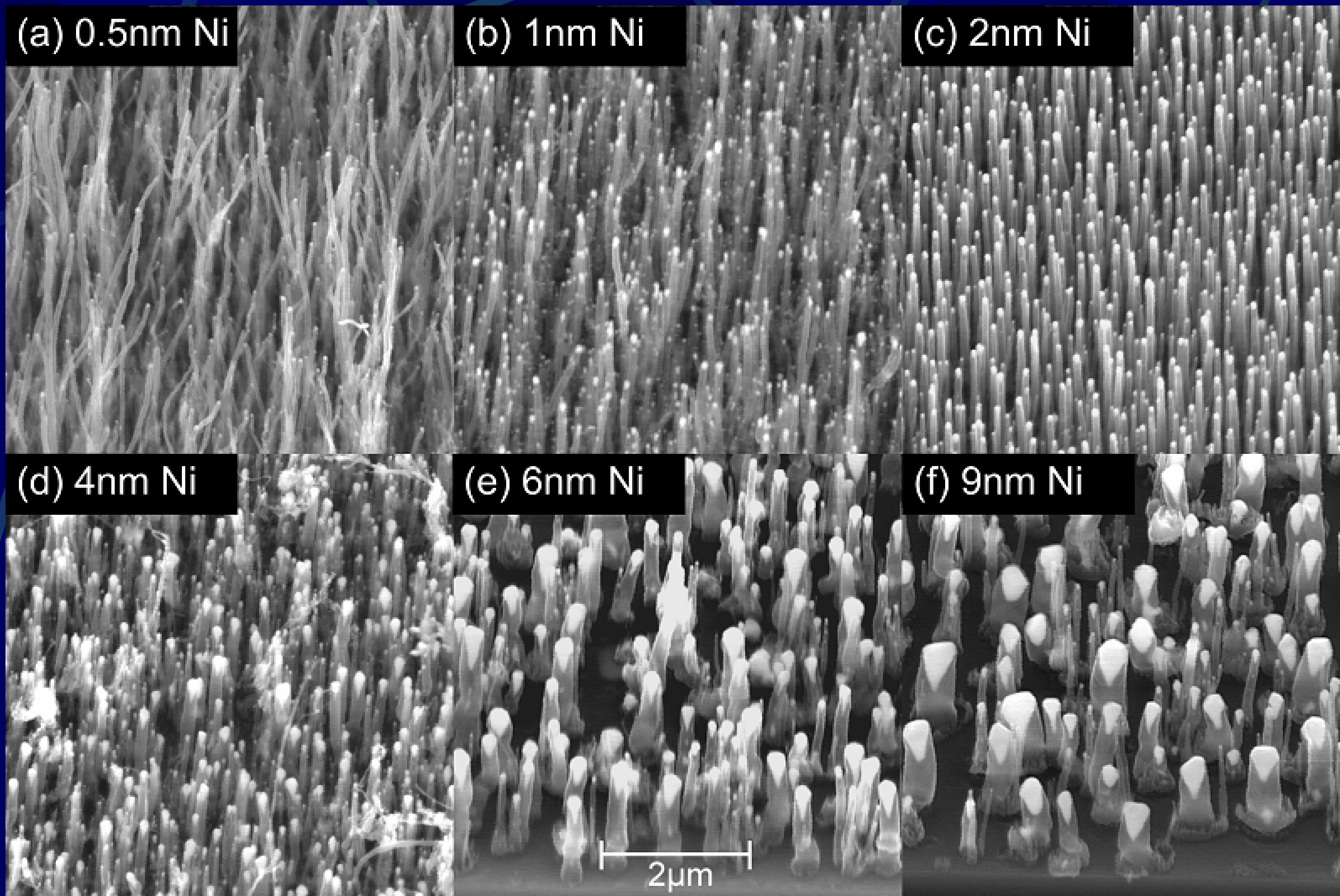
1. Decomposition of C_2H_2 by catalyst.
2. C dissolves and saturates in catalyst.
3. C precipitates as graphite tube.



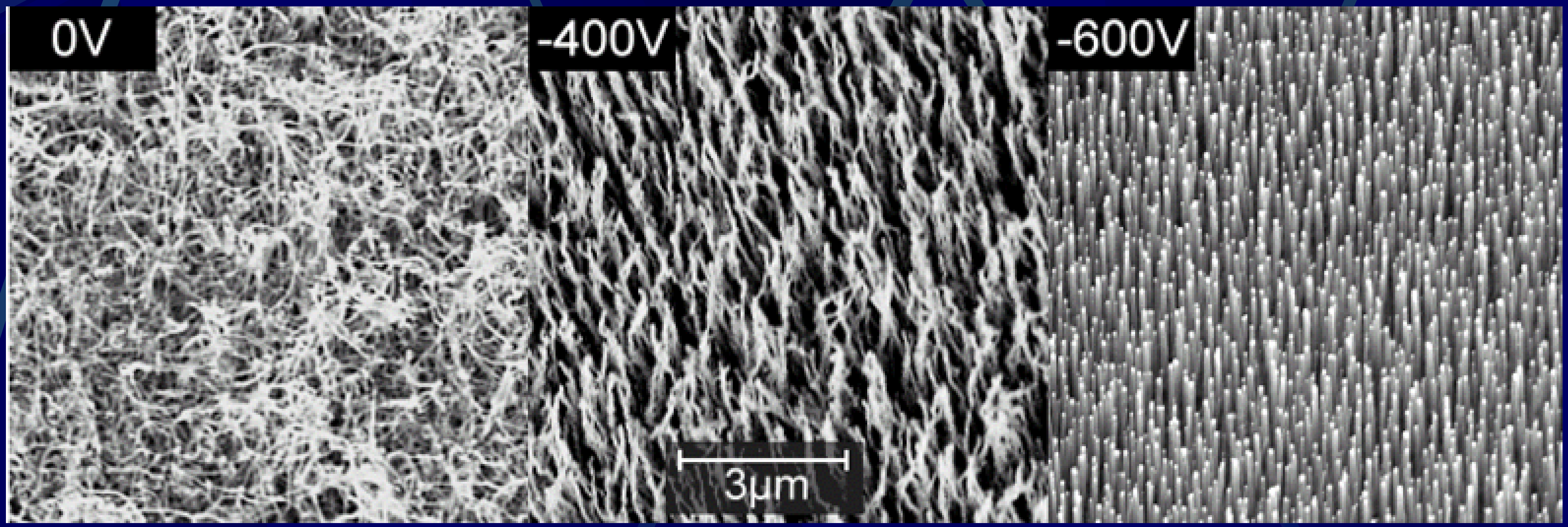
Ni nanoclusters Formed at 700°C



CNTs from Ni Nanoclusters

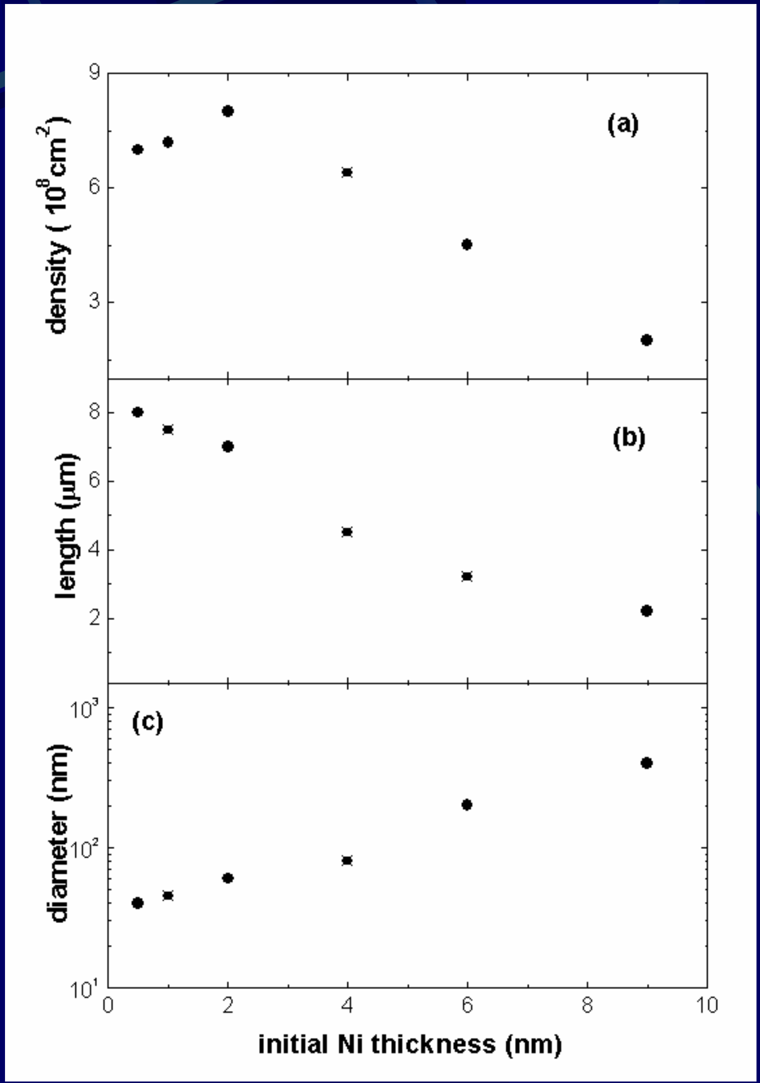


Influence of Plasma Bias Voltage on the Alignment of Nanotubes

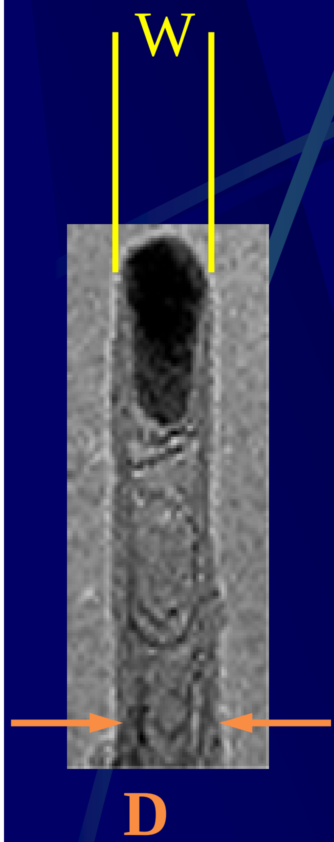


E = 0 V/μm   **E** = 0.1 V/μm   **E** = 0.35 V/μm

NT Properties vs. Initial Ni Thickness

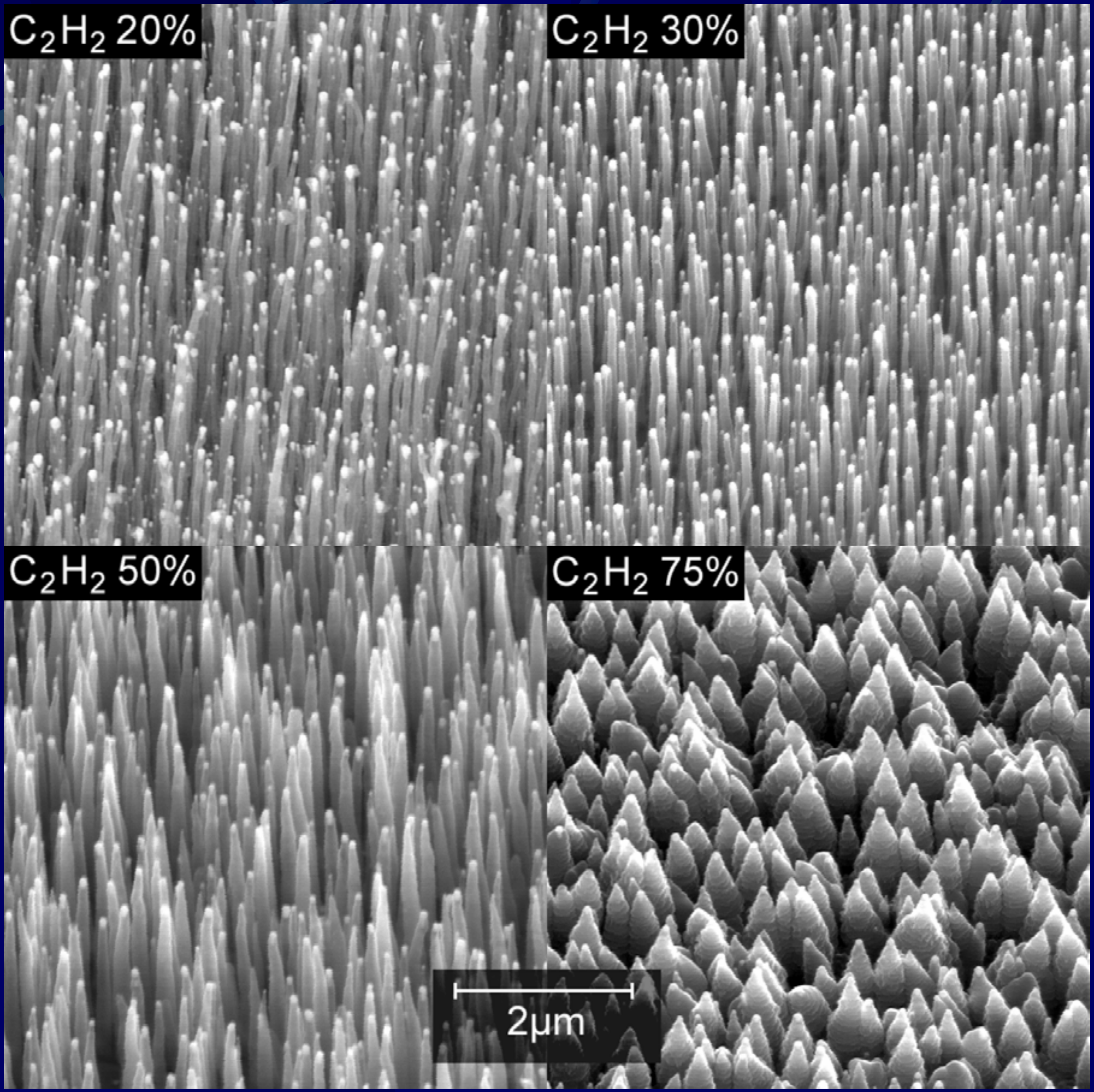


Correlation between tube diameter and catalyst particle width

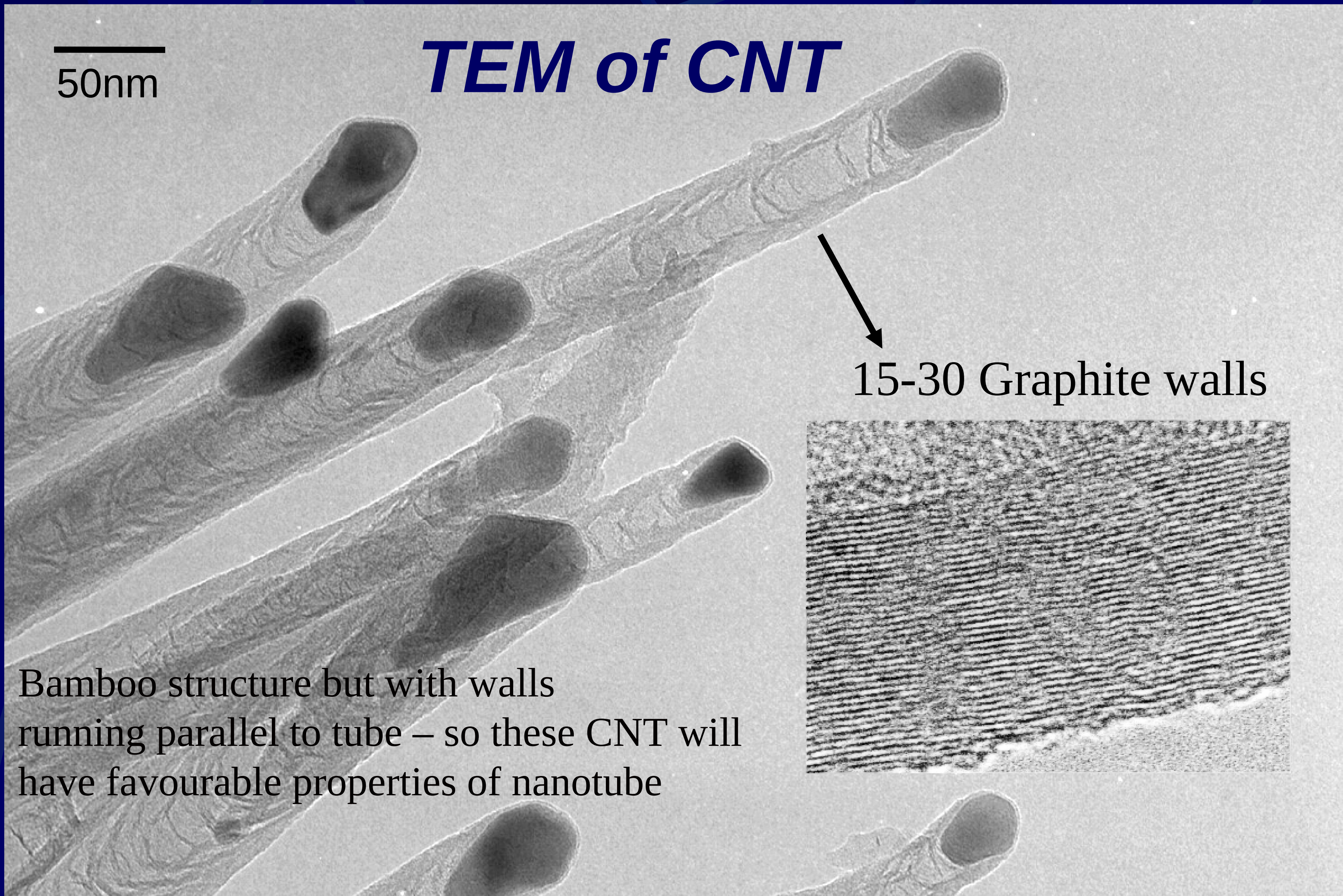


Substrate Temperature (°C)	Tube outer diameter (D) (average, nm)		Catalyst width (W) (average, nm)	
	PE	Thermal	PE	Thermal
550	32	15	30	5
700	45	25	45	12
850	100	75	100	75

Effect of $C_2H_2:NH_3$ gas ratio

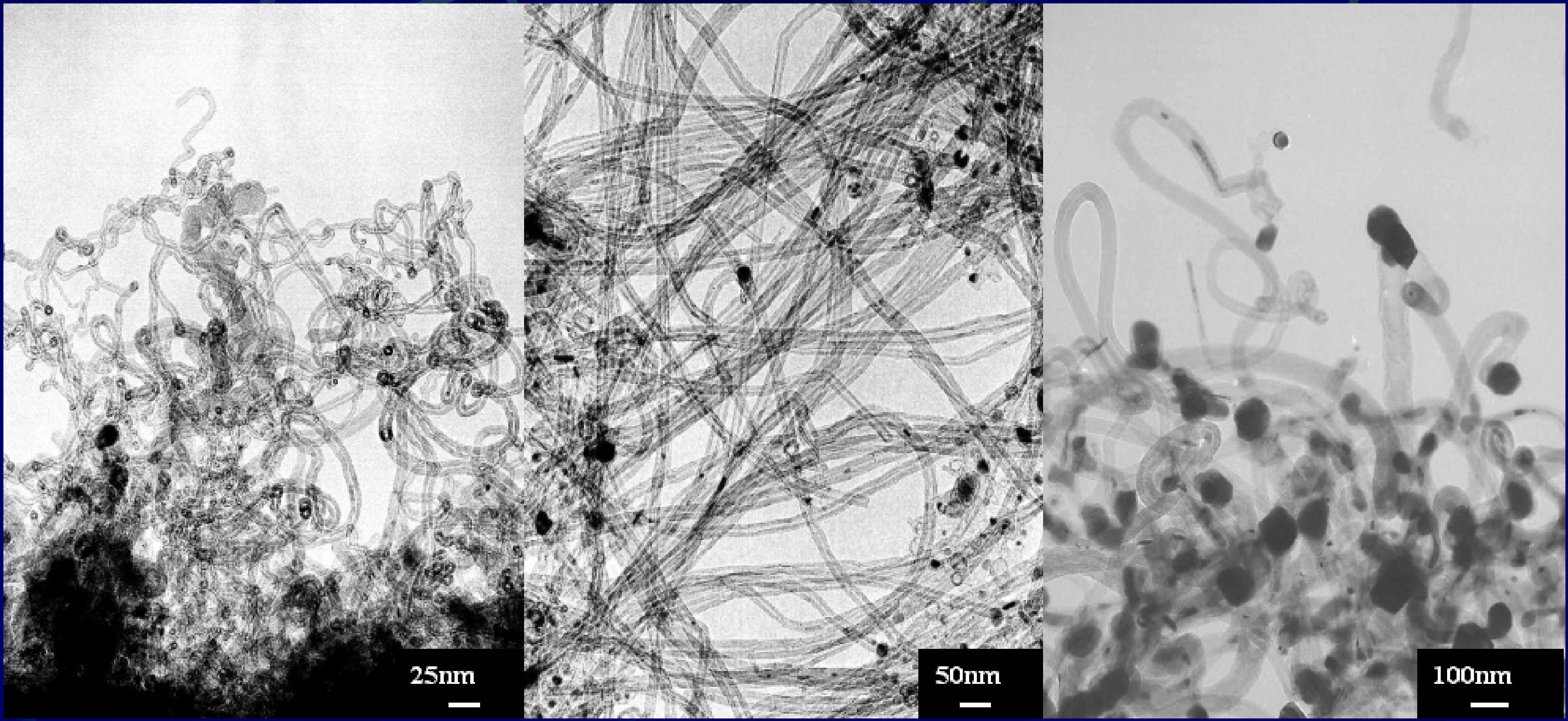


TEM of CNT



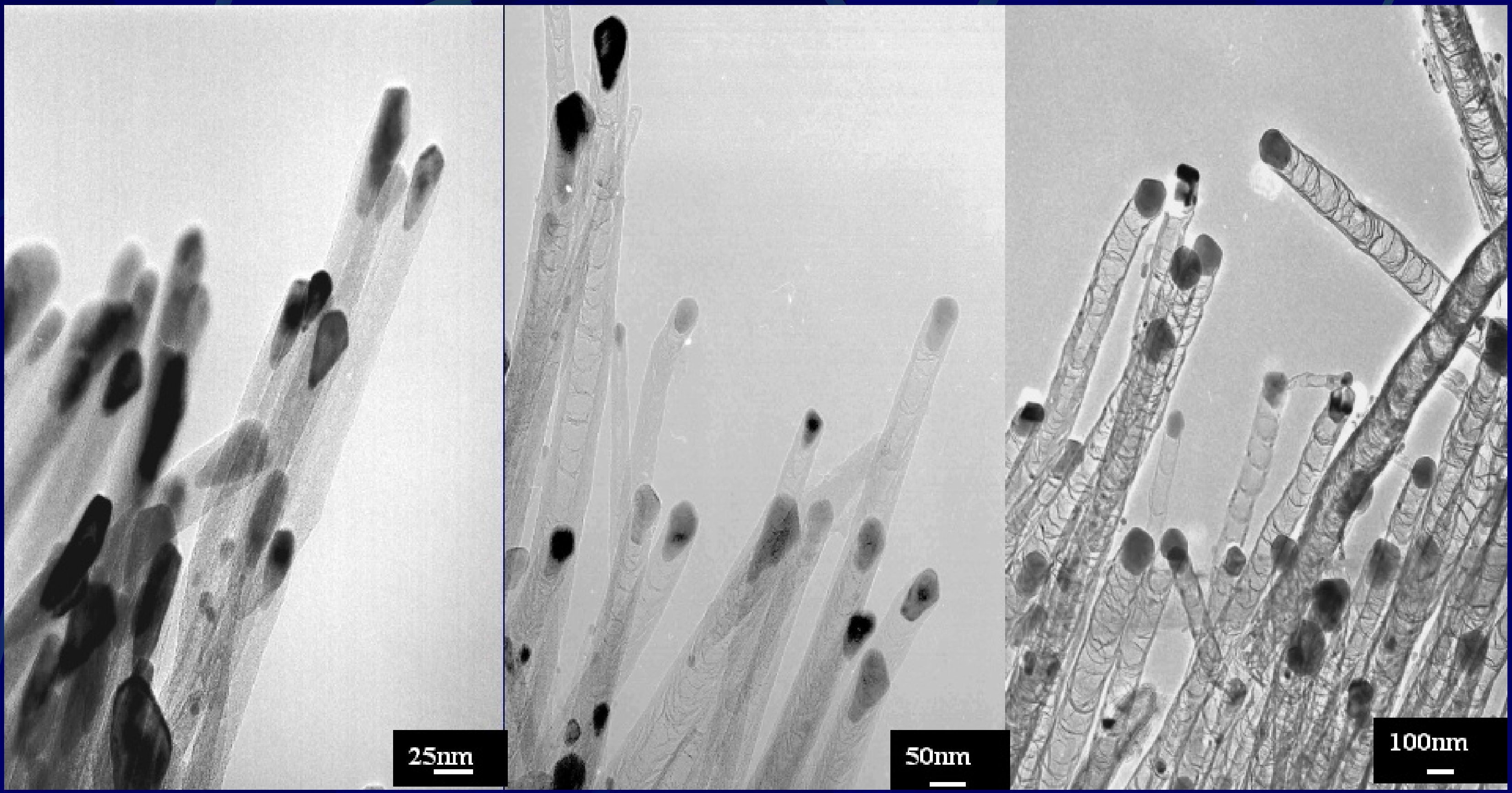
Bamboo structure but with walls running parallel to tube – so these CNT will have favourable properties of nanotube

Effect of Temperature (thermal CVD)



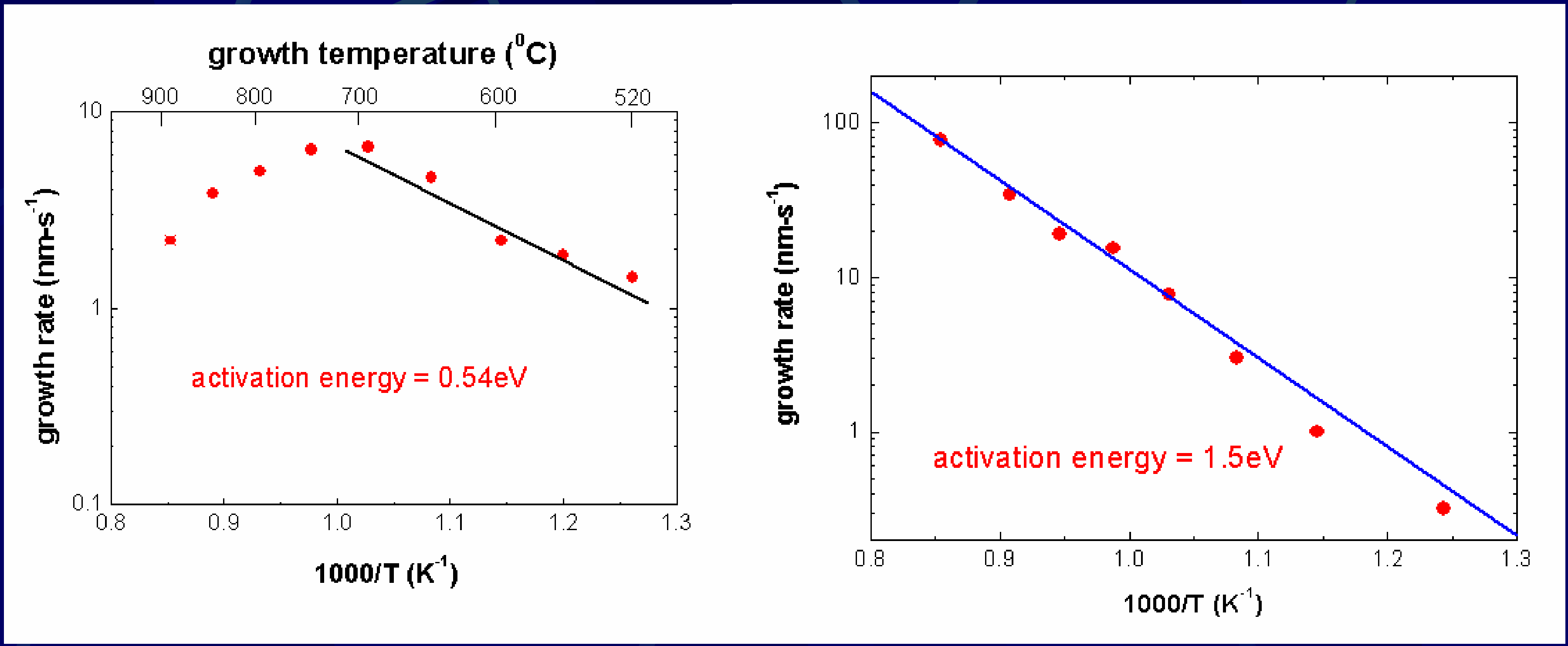
550°C 700°C 850°C

Effect of Temperature (PECVD)



550°C 700°C 850°C

Activation Energies

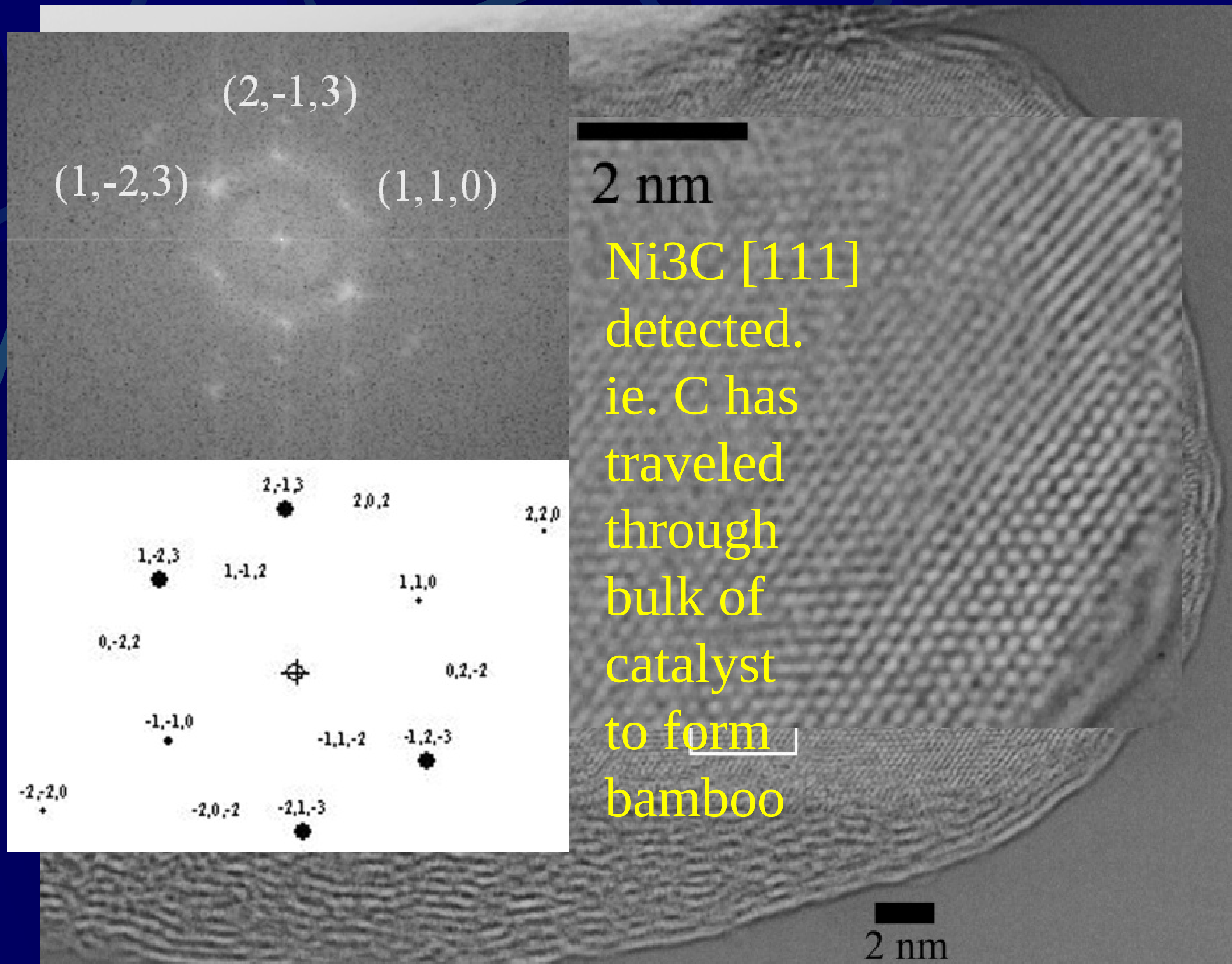


PECVD Growth

Thermal Growth

Energy barrier for C diffusion in Ni = 1.54eV

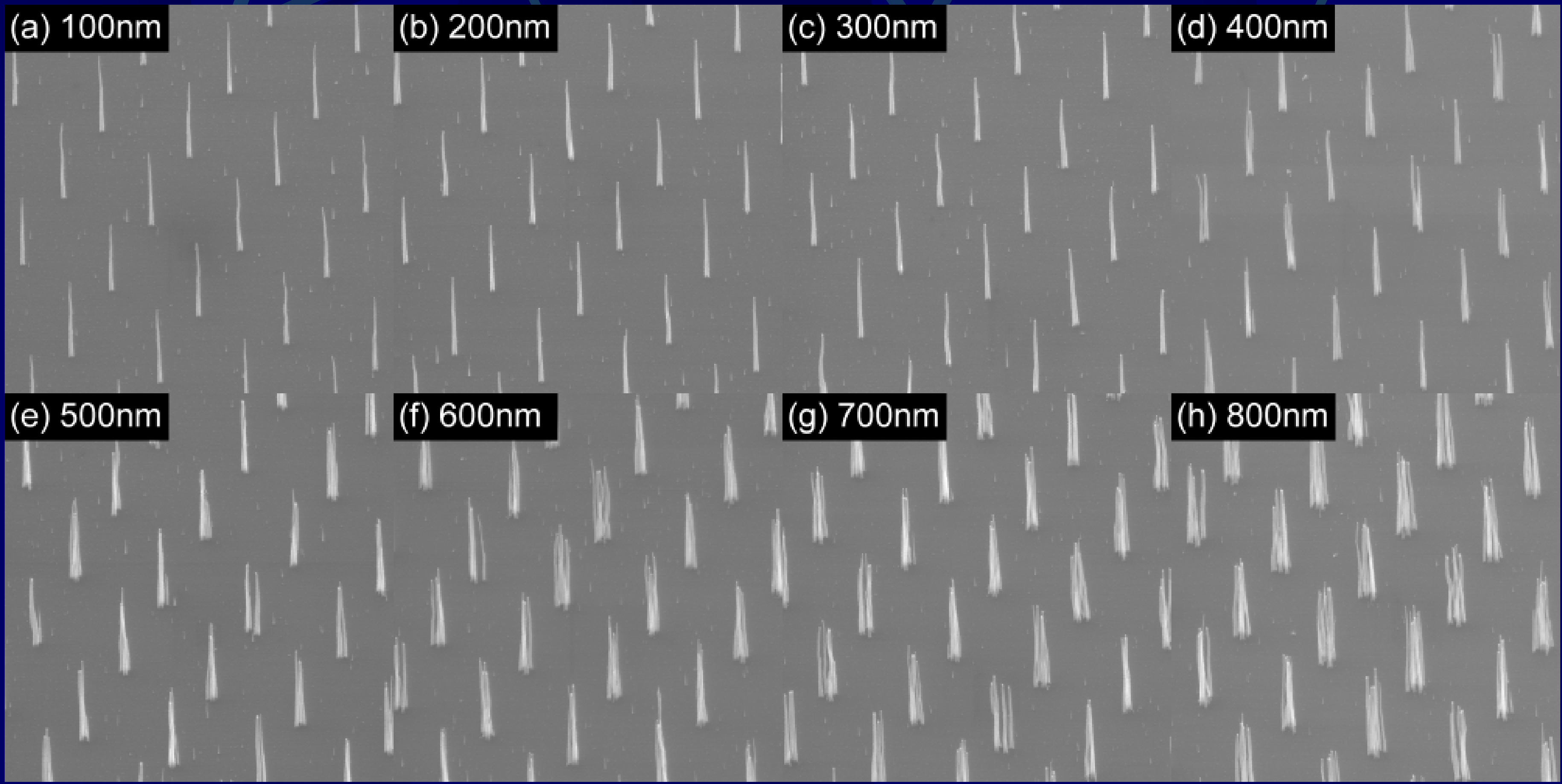
Why Bamboo?



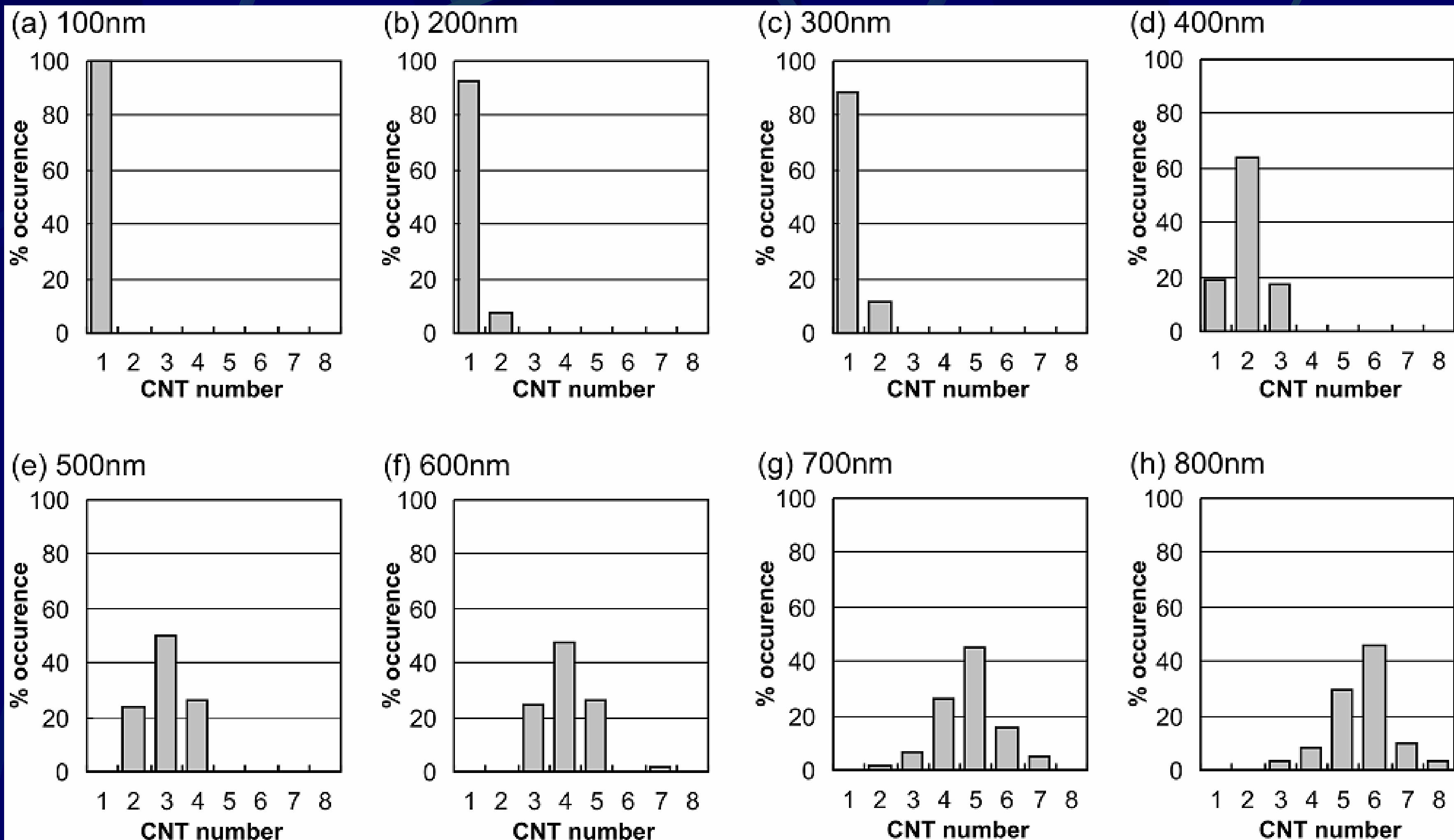
Ni3C [111] detected. ie. C has traveled through bulk of catalyst to form bamboo

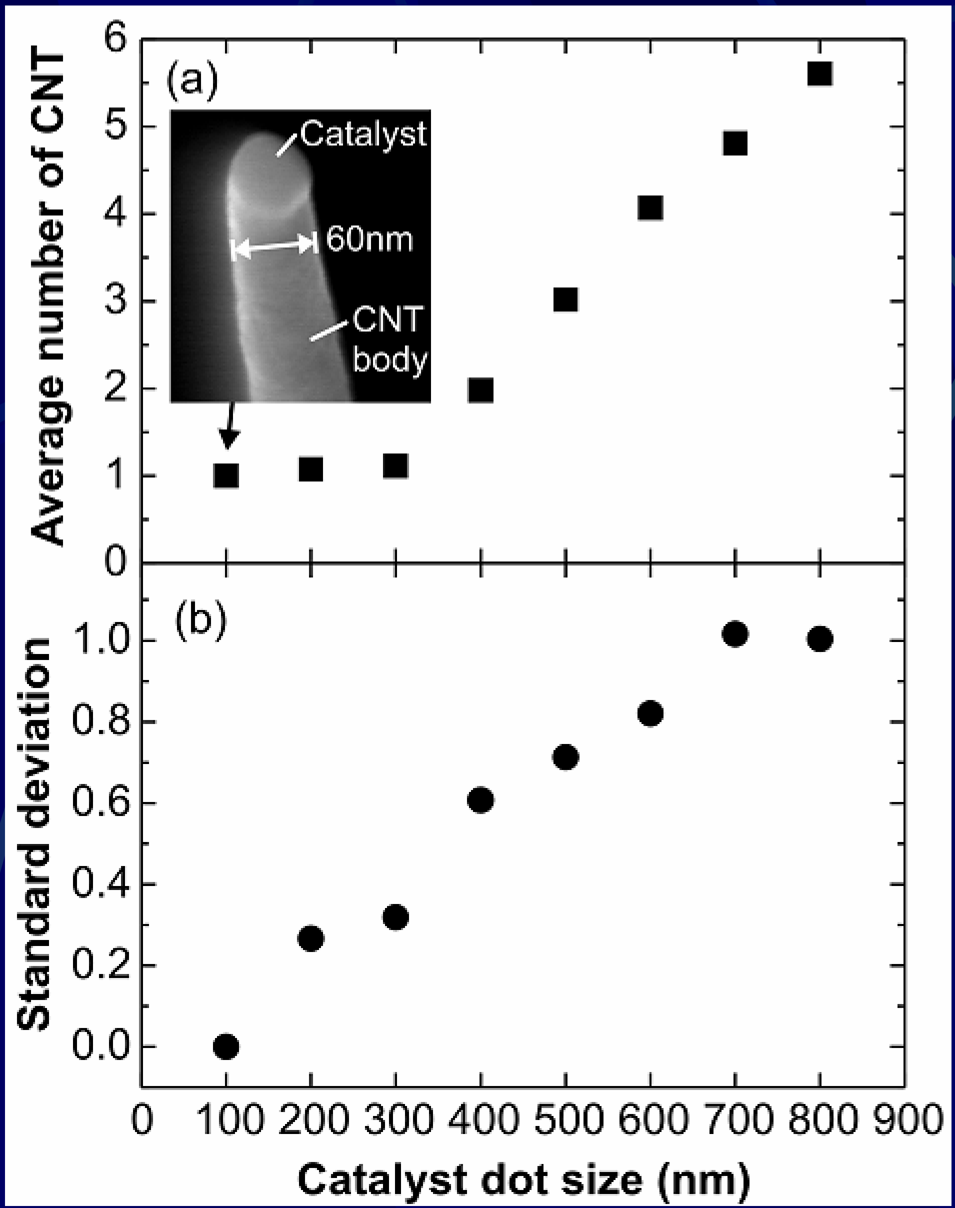
Litho. Conditions for Single CNT

- Fixed catalyst thickness (8nm), catalyst dot width varied.



Number of CNT per catalyst dot





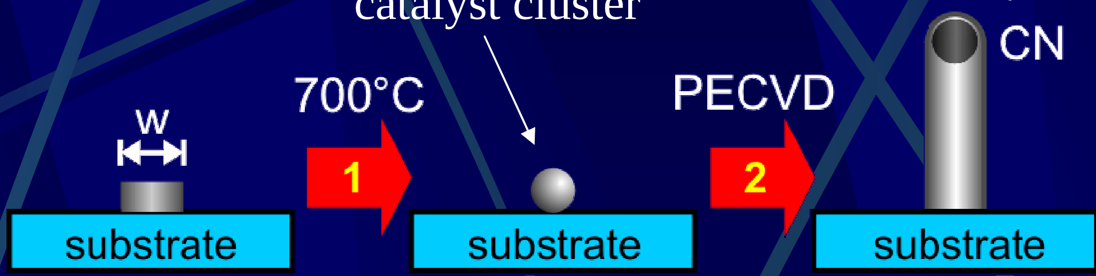
- Avg. number of CNT increases at 1 CNT per 91nm of dot size.
- Std. Dev. increases with dot size.
- Catalyst is conserved

ie. $100 \times 100 \times 8 = (4/3)\pi r^3$

$\therefore$ r = 27nm

c.f. measured r = 30nm

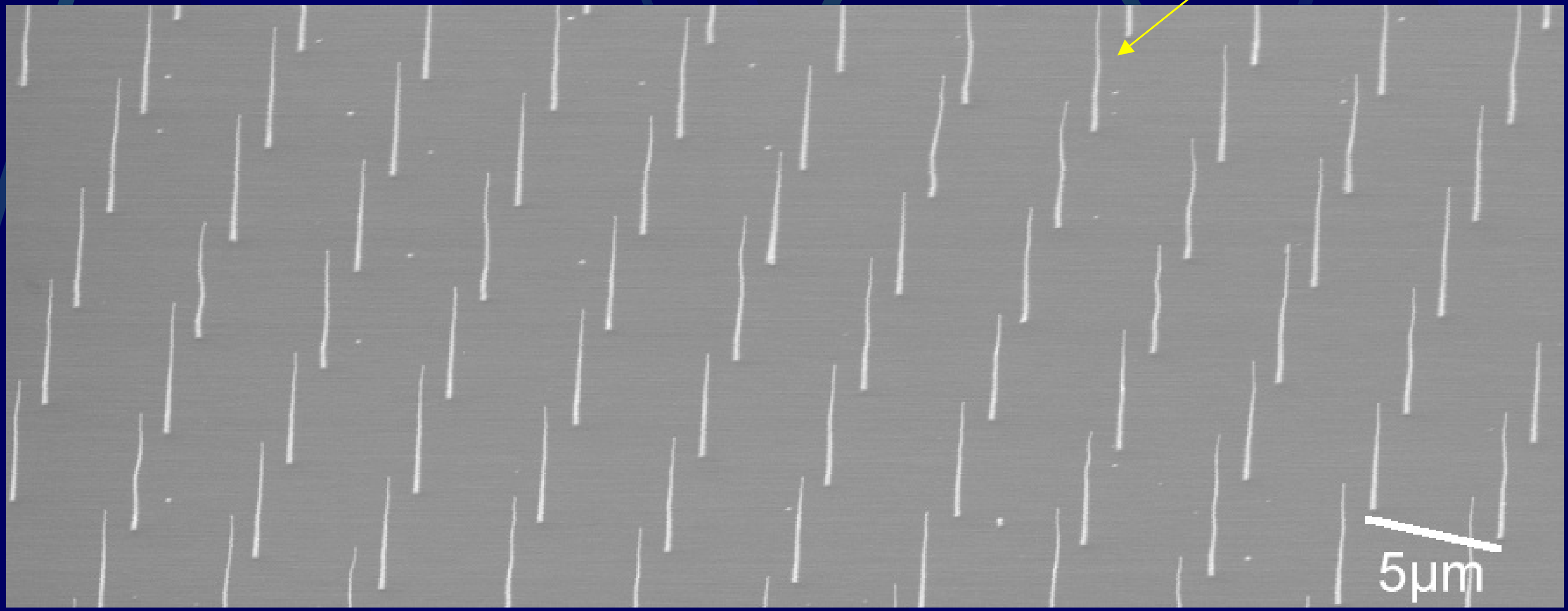
Ultimate control of CNT growth



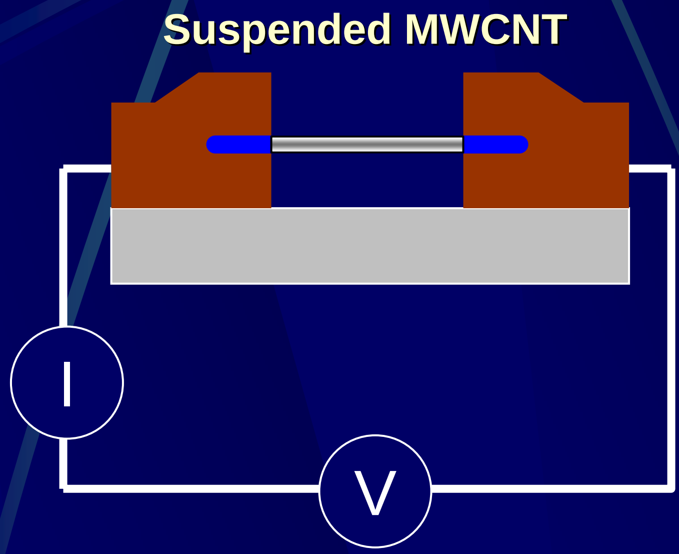
Single, fixed size catalyst cluster

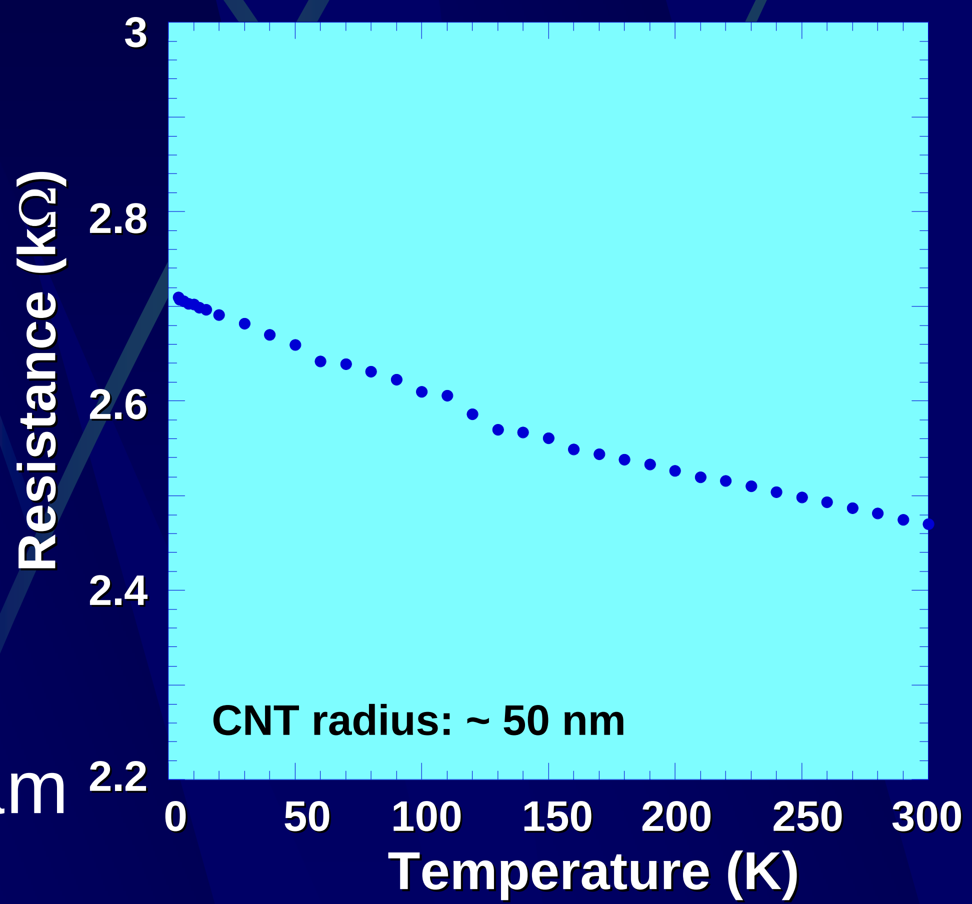
Single CN of fixed diameter. Height Controlled by deposition time.

Std dev diameter = 4.1%
Std dev height = 6.3%



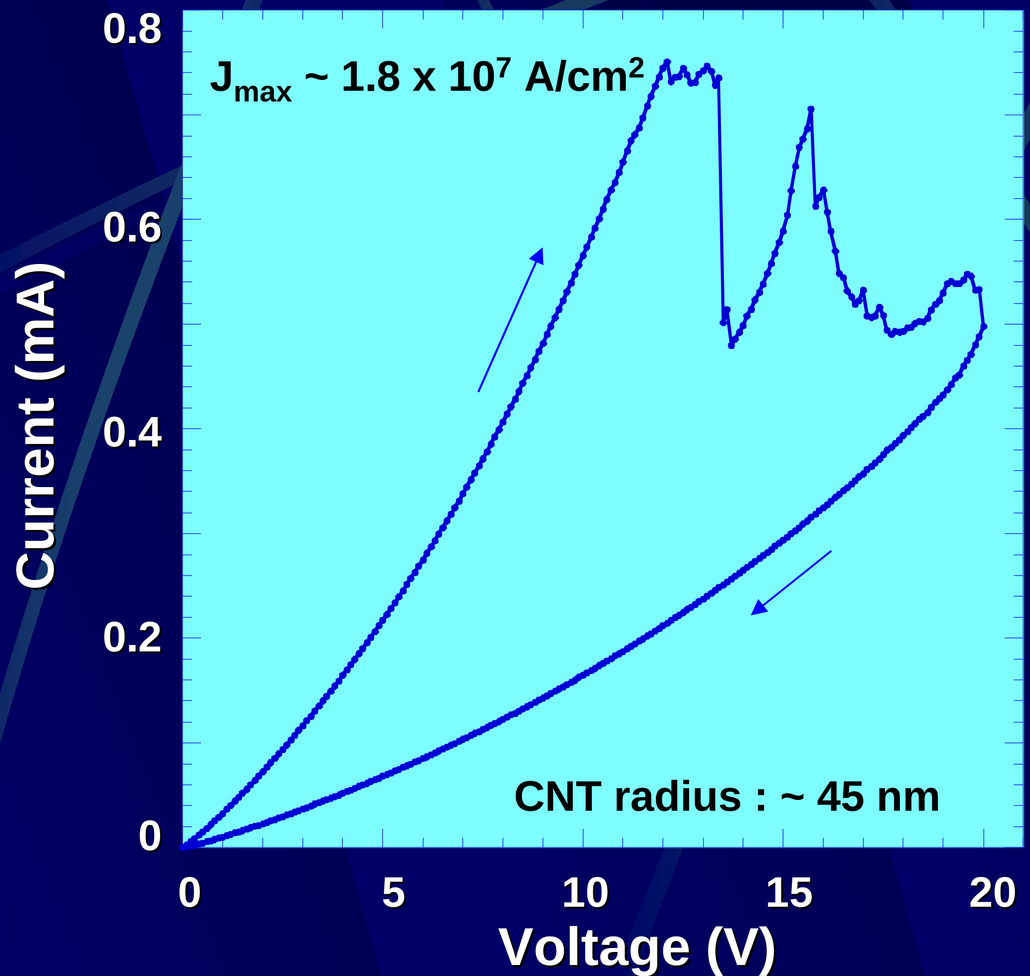
Electrical Characteristics of CNT

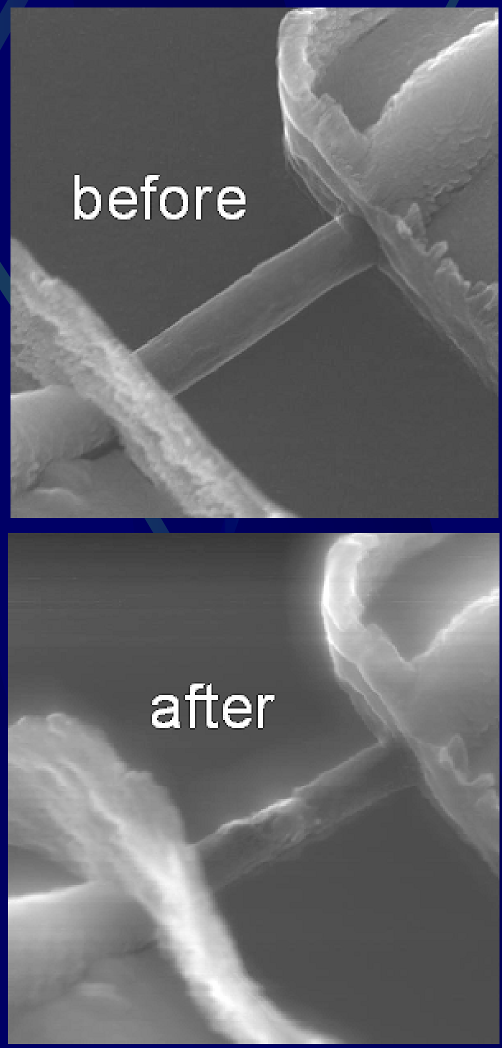




R_{CNT} ~ 1-10 kΩ per µm
ρ_{CNT} ~ 10^{-6}-10^{-5} Ωm

Electrical Breakdown of CNT

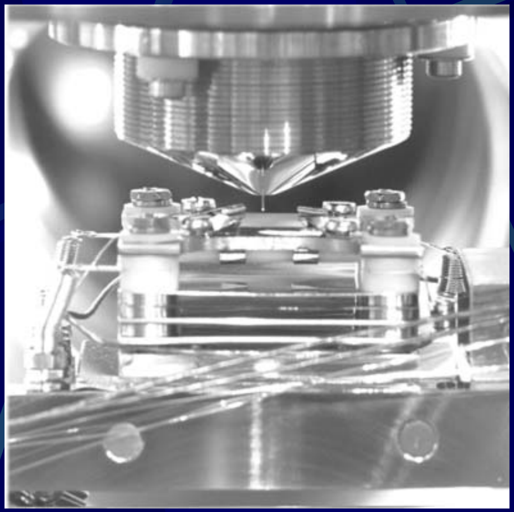


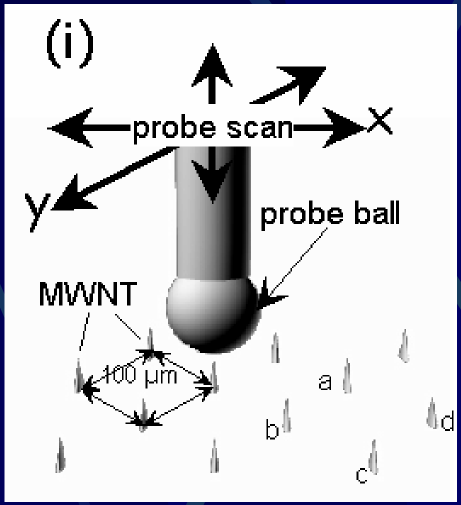


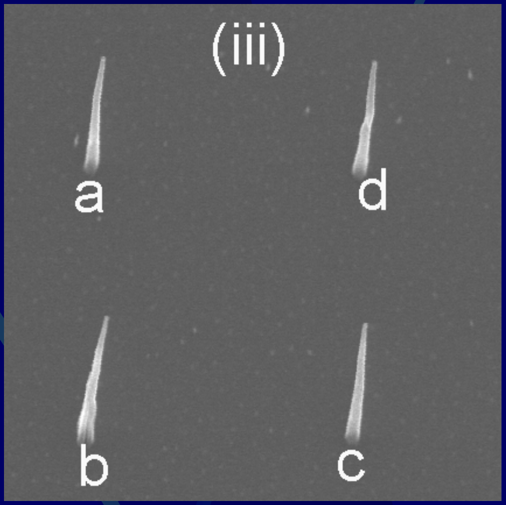
Max $J_{CNT} = 10^7 – 10^8 A/cm^2$

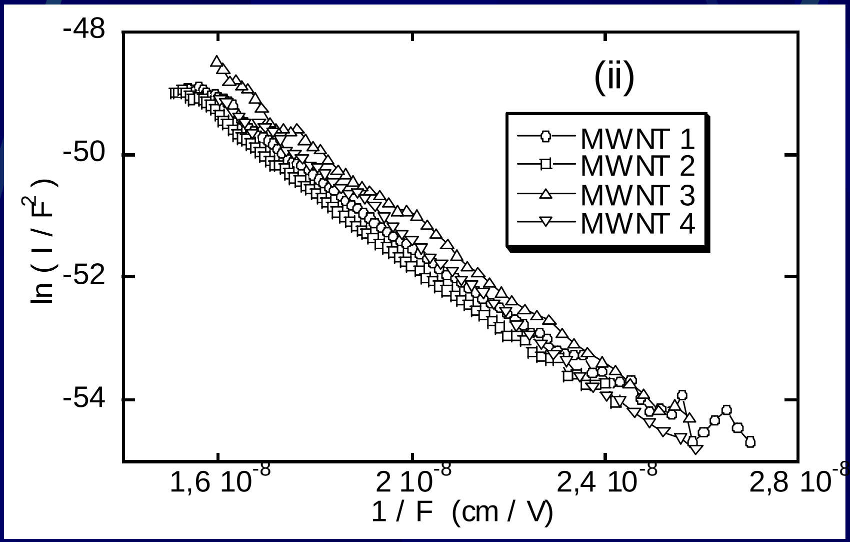
FE properties of individual CNTs

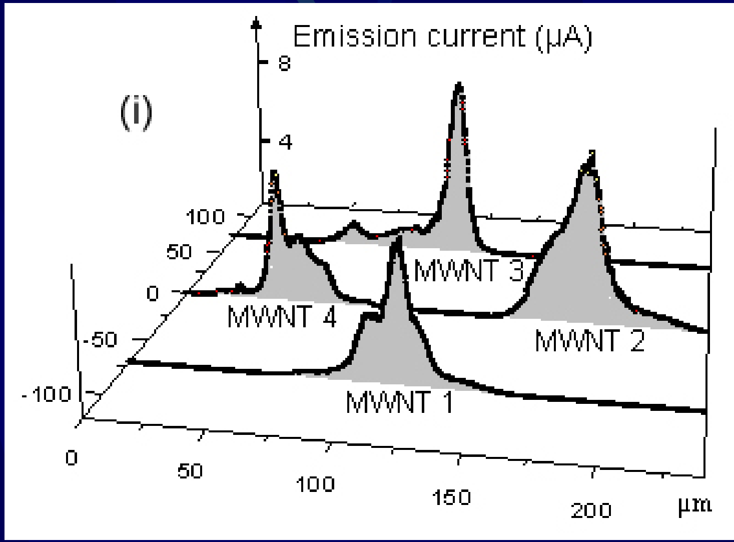
In collaboration with Binh et al



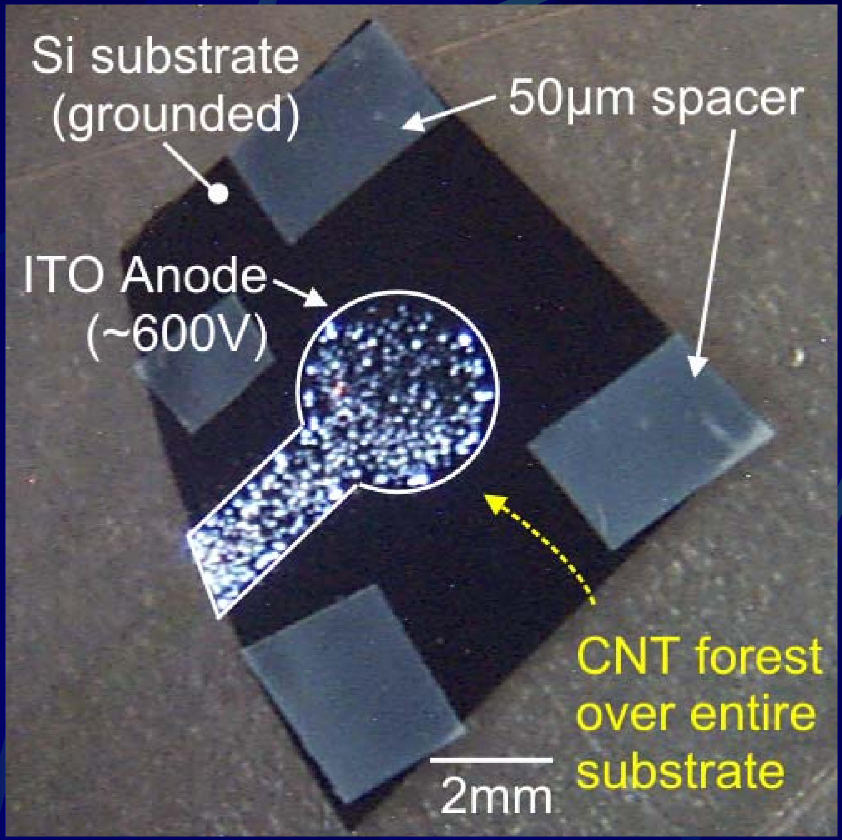




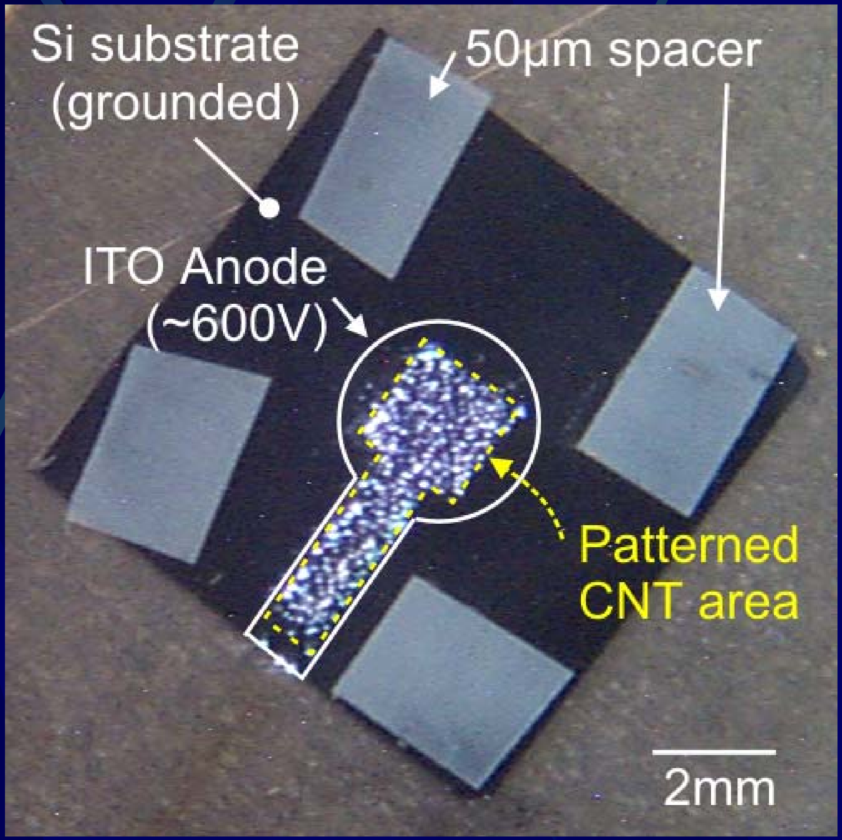




Emission site density

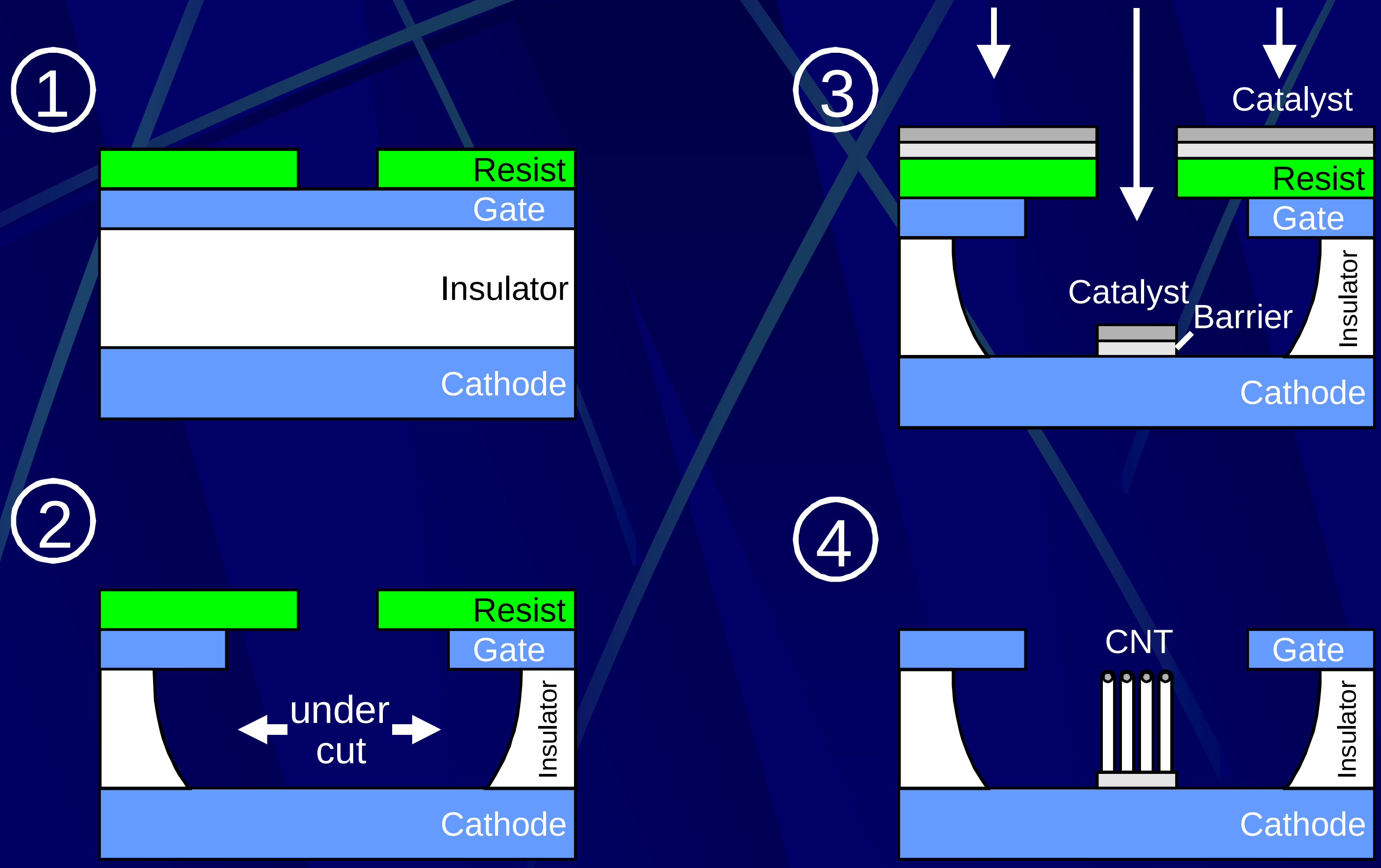


Dense CNT forest
(ESD=10^3/cm^2)

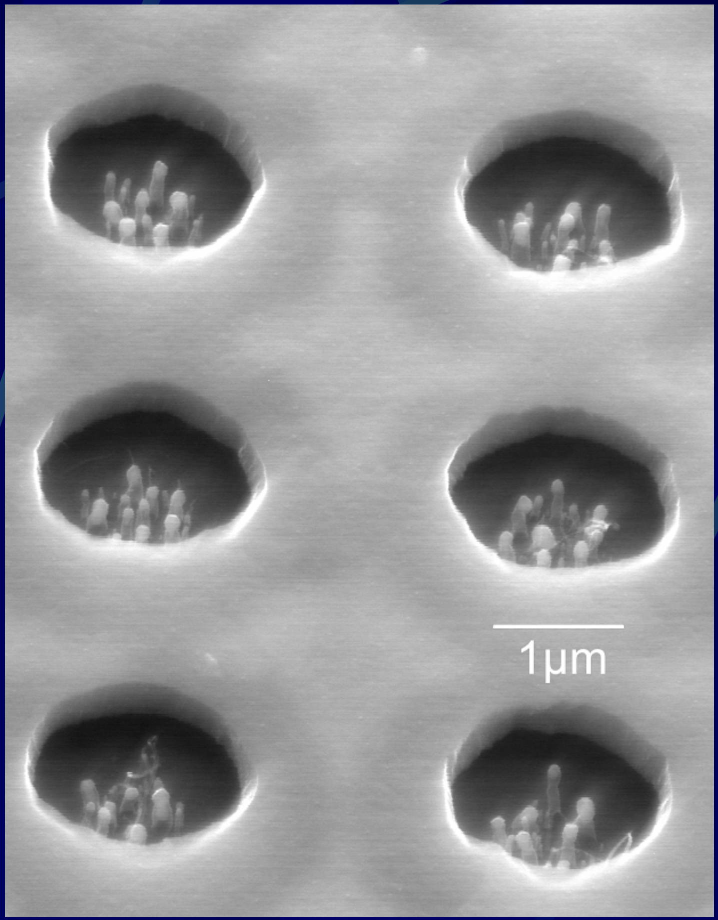


Array of CNT
(ESD=10^4/cm^2)

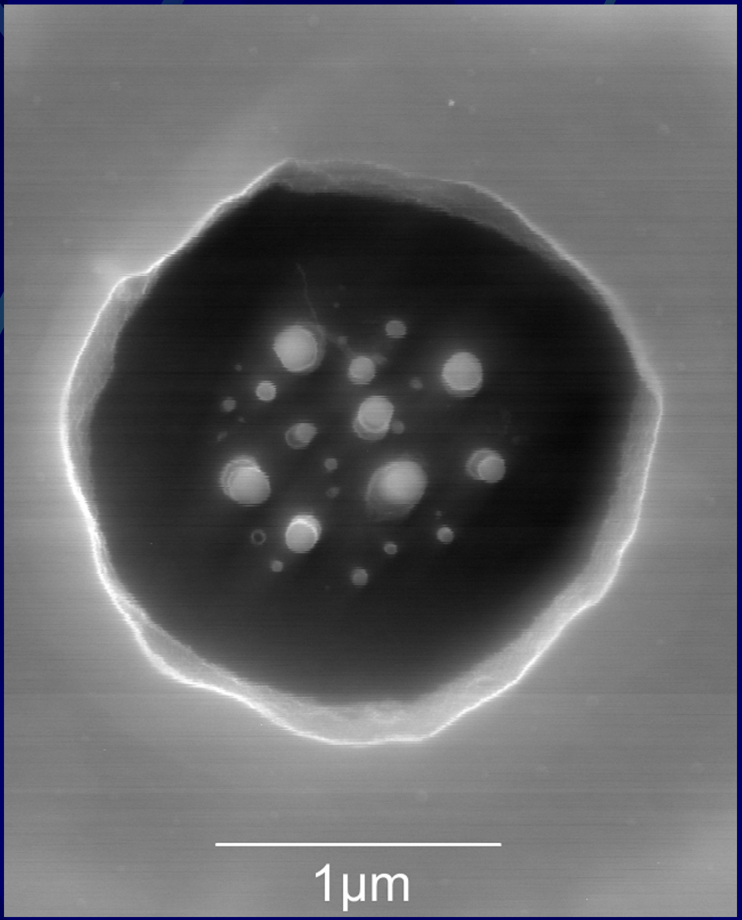
Self-aligned Microcathode Fabrication



CNT Microcathode

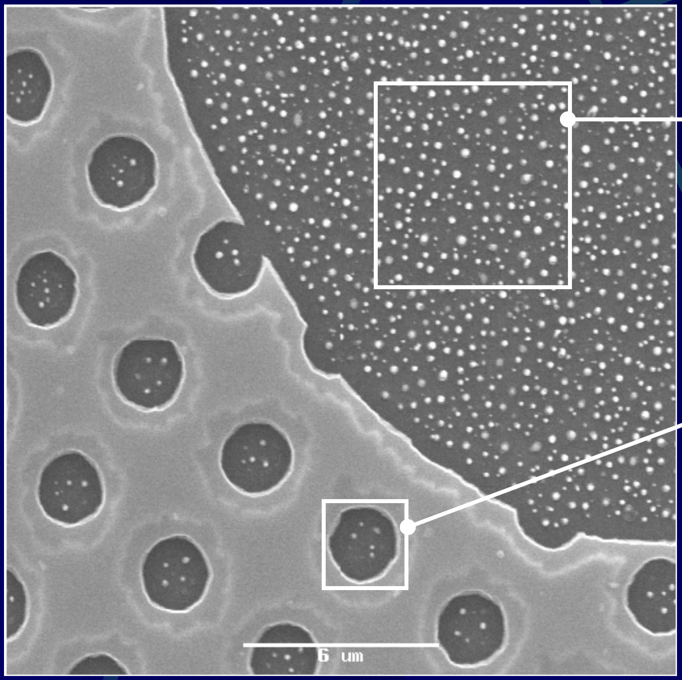


Tilted view



Top view

Density Control of CNT

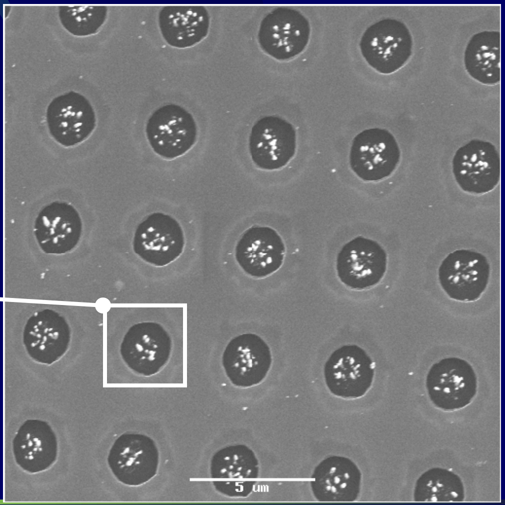


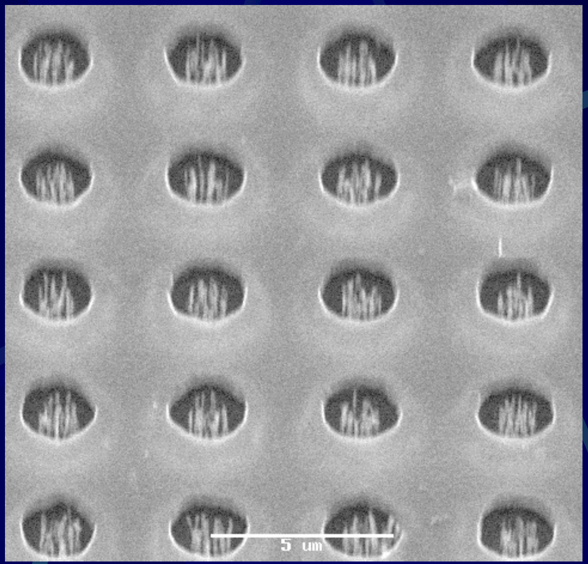
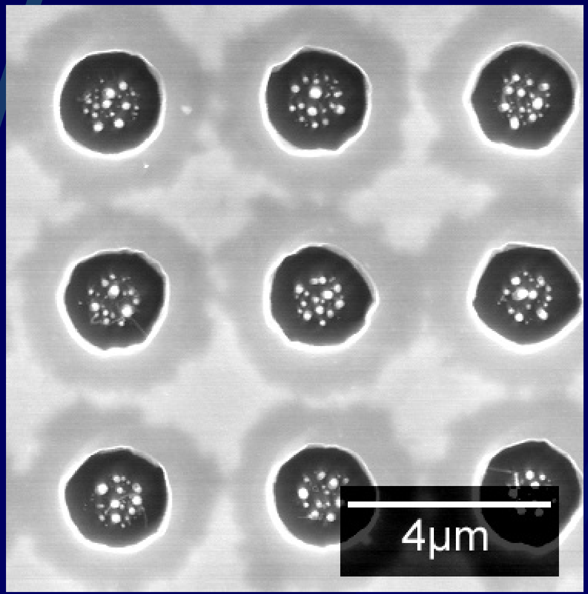
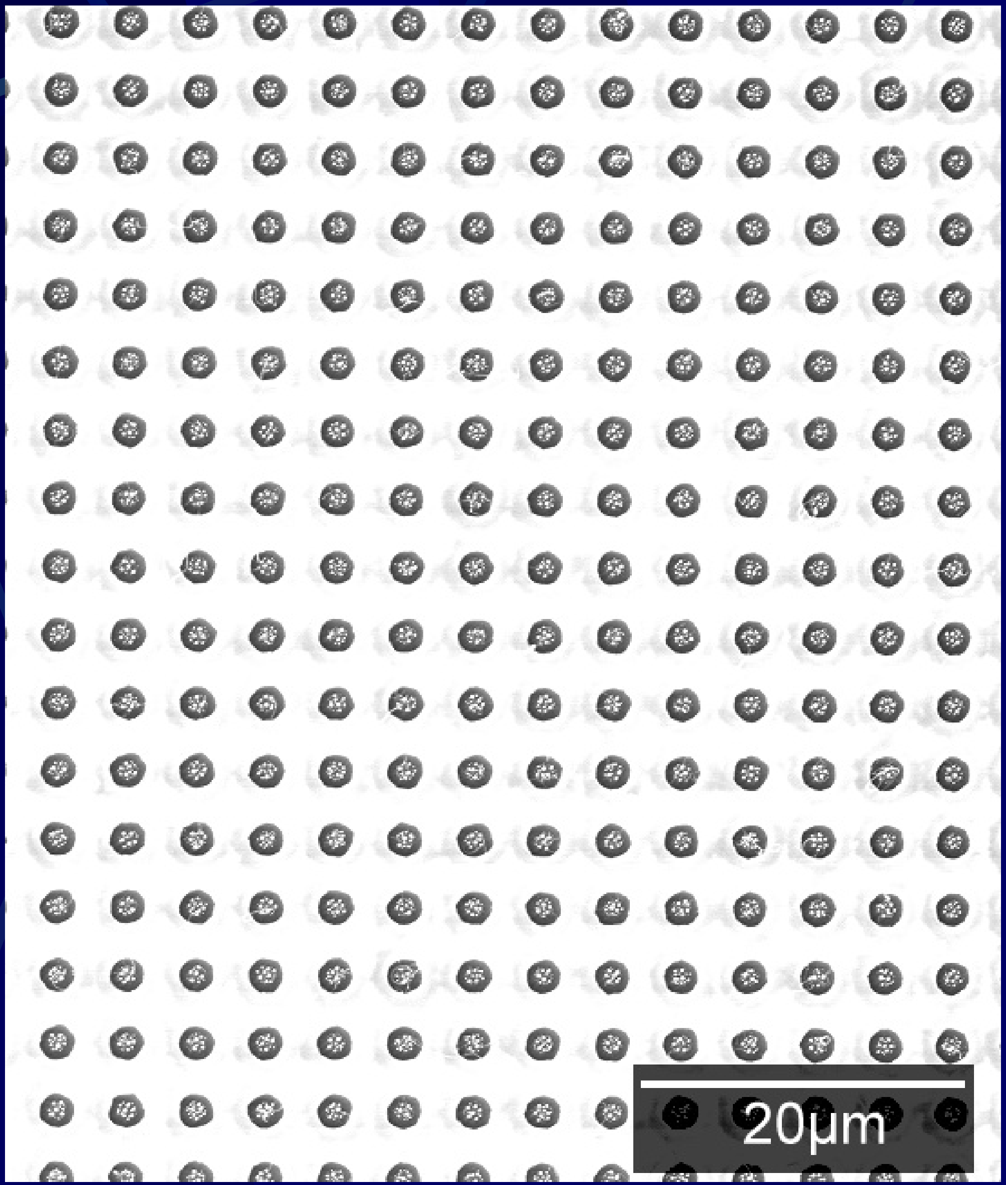
SEM top view

$5x10^8$ nanotubes per cm^2
should lead to

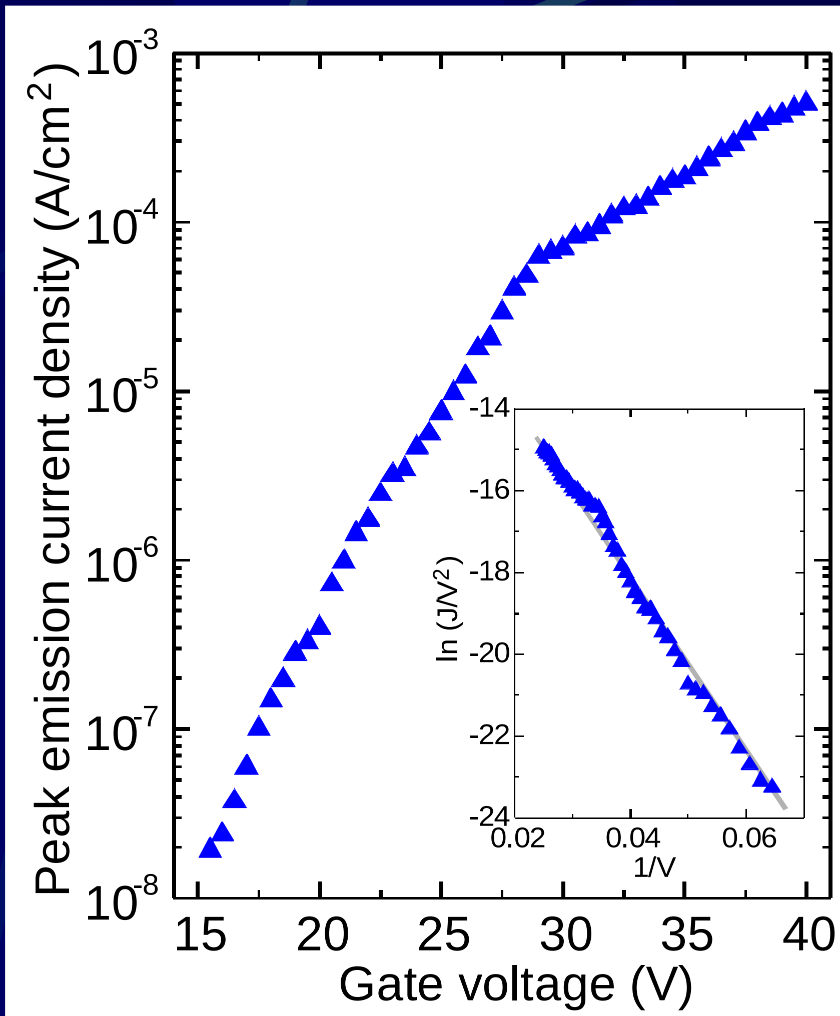
4 to 5 nanotubes in
a 1 µm diameter dot

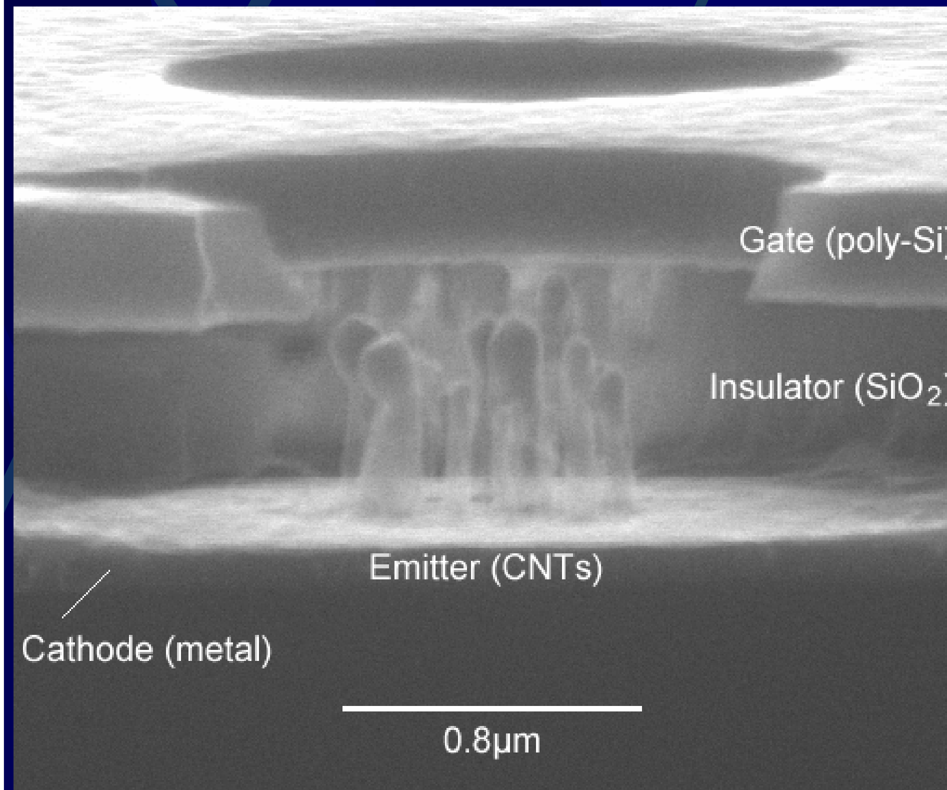
Growth with $1x10^9$ per cm^2
8 to 10 CNTs per dot




5 um

4μm

20μm

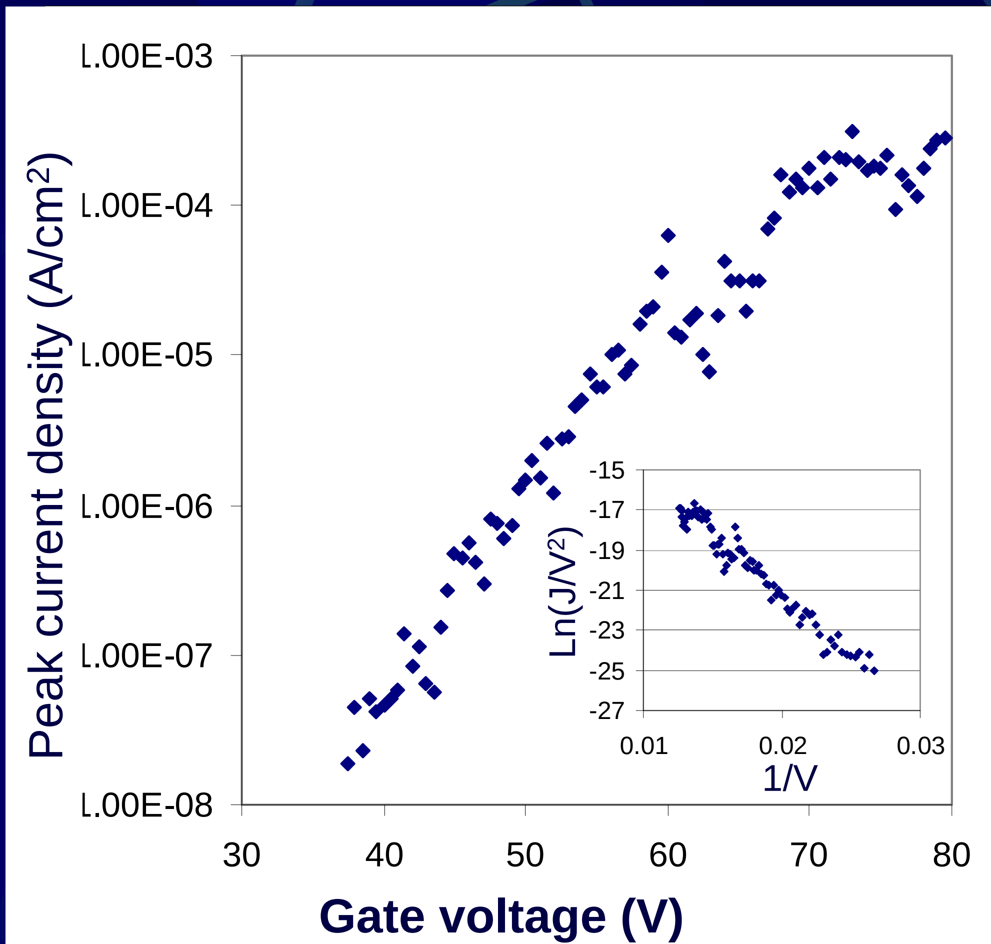
Field Emission of CNT Cathode

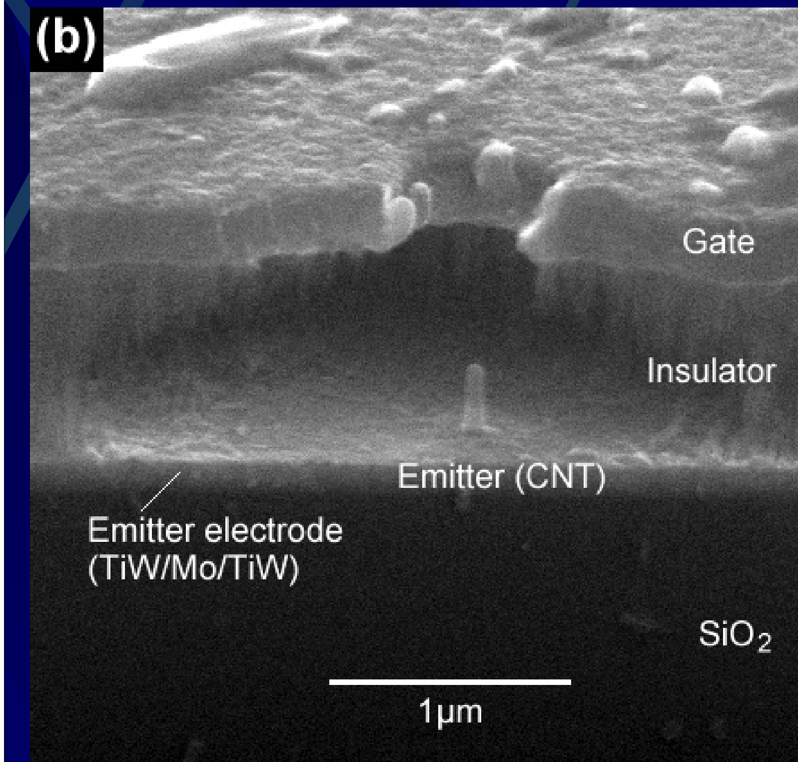




Cross-section

Field Emission of CNT cathode





Cross-section

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Future Potential?

- Multiwall CNTs (eg. by PECVD) appear to be well suited for field emission applications.
- Issues to be addressed now: Cost effectiveness and lifetime.