Science and Technology of Advanced Multifunctional Nanocarbons for Vacuum Microelectronics

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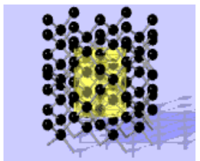
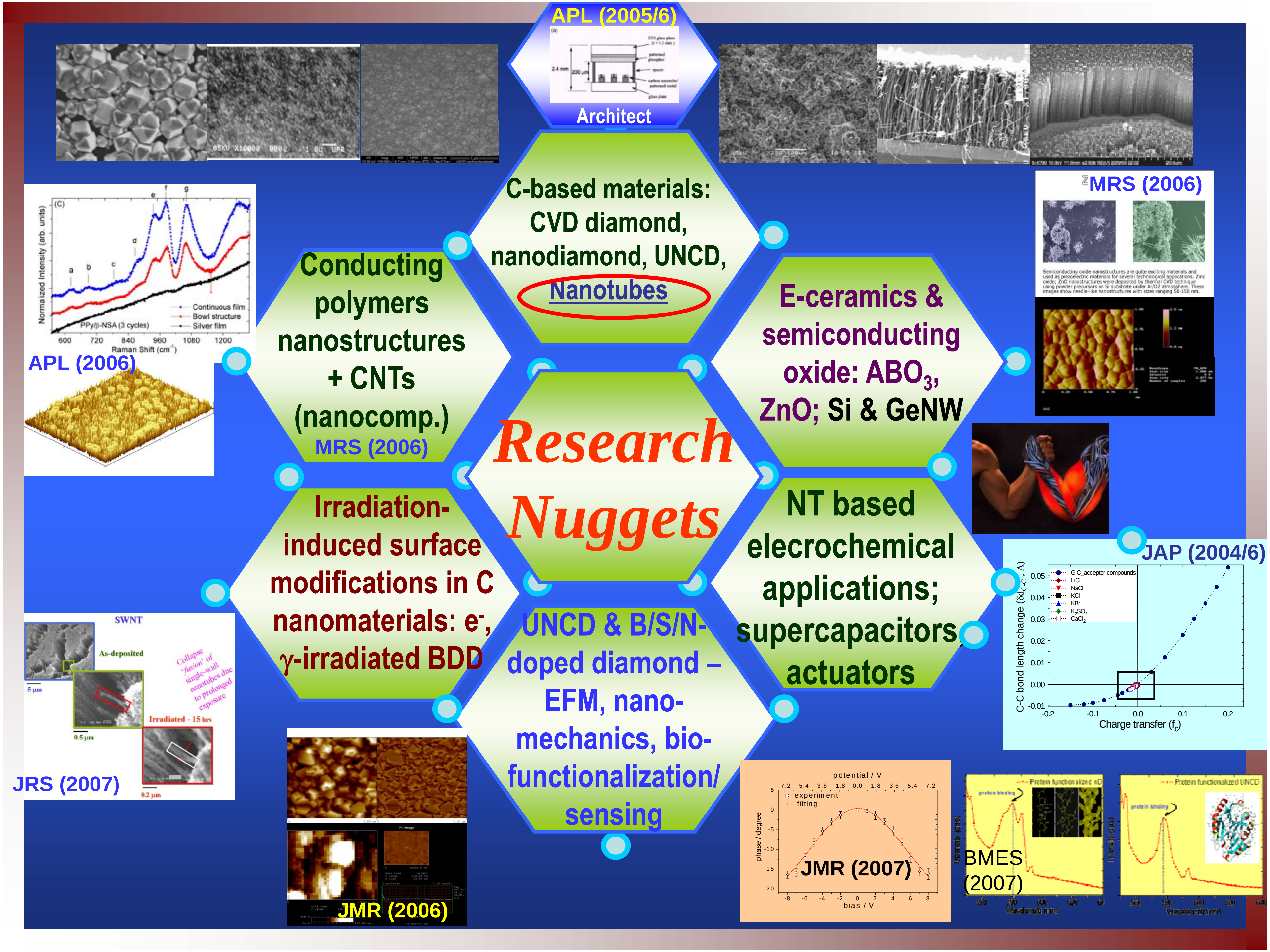
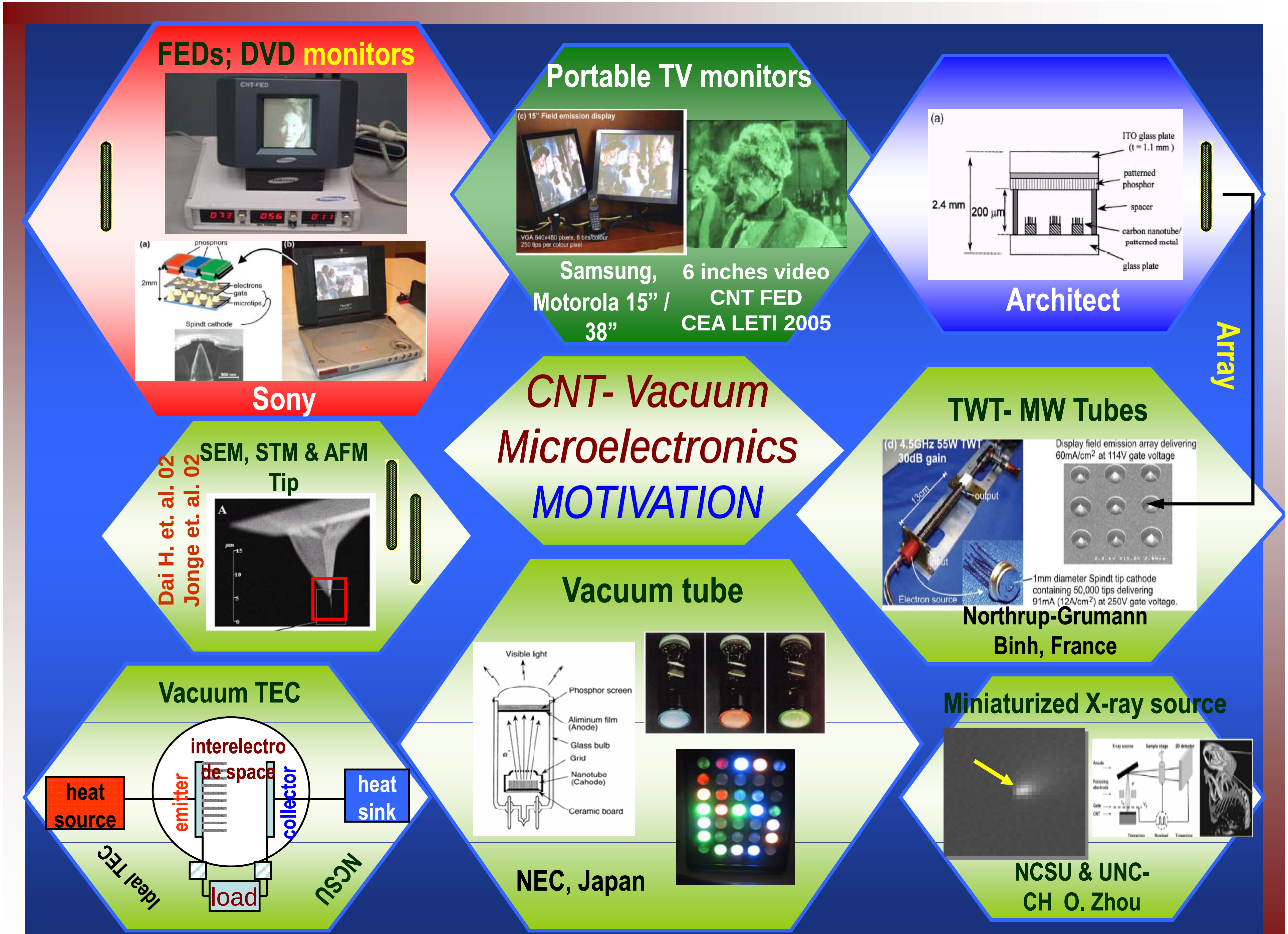


U. Tokyo Visit - Dec. 26, 2007 @ 2.00 PM



APL (2005/6)
Architect
C-based materials: CVD diamond, nanodiamond, UNCD, Nanotubes
Conducting polymers nanostructures + CNTs (nanocomp.)
MRS (2006)
E-ceramics & semiconducting oxide: ABO3, ZnO; Si & GeNW
Research Nuggets
Irradiation-induced surface modifications in C nanomaterials: e-, γ-irradiated BDD
NT based elecrochemical applications; supercapacitors, actuators
UNCD & B/S/N-doped diamond – EFM, nano-mechanics, bio-functionalization/ sensing
APL (2006)
MRS (2006)
JAP (2004/6)
JRS (2007)
SWNT
As-deposited
Irradiated - 15 hrs
Collapse 'fusion' of single-wall nanotubes due to prolonged exposure
JMR (2006)
JMR (2007)
BMES (2007)
Continuous film
Bowl structure
Silver film
PPy/β-NSA (3 cycles)
Raman Shift (cm-1)
Normalized Intensity (arb. units)
C-C bond length change
Charge transfer (fc)
GIC_acceptor compounds
LiCl
NaCl
KCl
KBr
K2SO4
CaCl2
potential / V
phase / degree
bias / V
experiment
fitting
Protein functionalized UNCD
protein binding



Chem. Mater. **14** (2004).

PART I

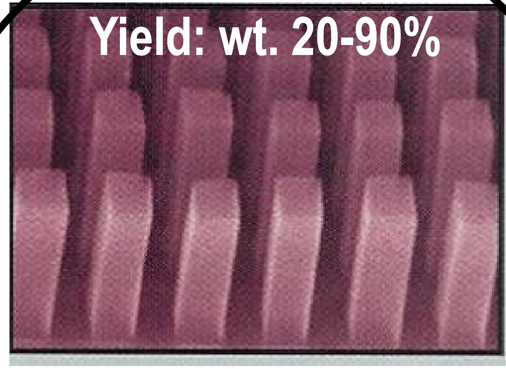
VACNTs Films Using MPACVD: Single-/Double- and Multiwalled; Synthesis and Characterization

- synthesis; optimized growth

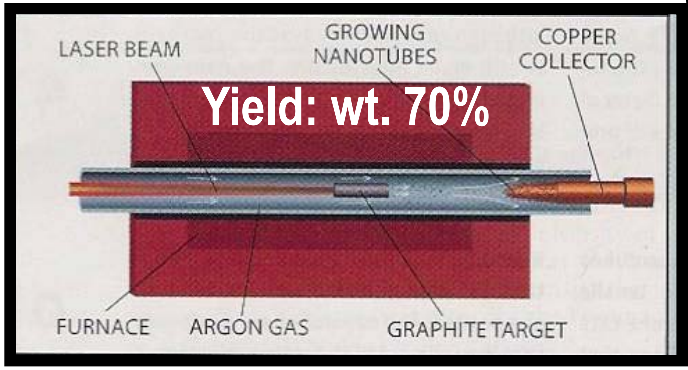
- diameter (small vs. large)
- growth mechanism: root vs. tip
- impurity
- catalyst (shape, size, type)
- orientation (V vs H)
- technique (thermal, PLV, PE)
- length (short vs. long)
- support (substrate)
- specificity (random vs. patterned)
- chirality
- functional nanostructures

Ways to make Nanotubes:

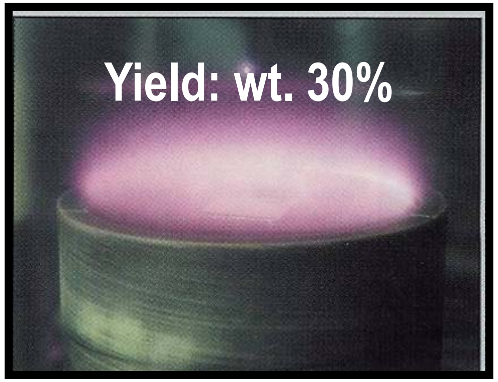
Zap, Bake or Blast



A hot gas-CVD @ Duke, Stanford, Cornell, and Japan - Endo



A laser blast @ Rice: Smalley



[A big spark- DC arc discharge @NEC, Japan - Iijima]

Thermal, Plasma-enhanced CVD -

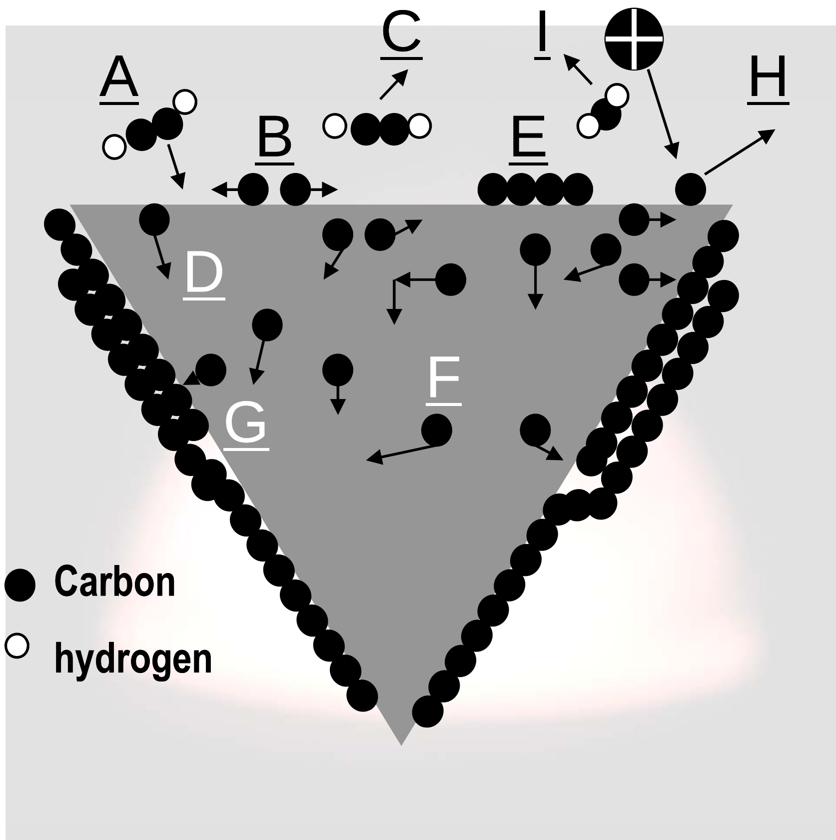
DC, RF, ECR, MW

Physico-chemical processes

Processes and characteristic energies in nucleation and growth on surfaces

'kinetic *versus* thermodynamic control'

$xC_2H_2 + NH_3 \rightarrow C + NH_3^{+*} + (x/2)H_2^{n+*}$



A: *arrival* of excited species to the surface

B: catalytic *dissociation*

C: *departure* of undissociated molecules

D: *solution* of C into the catalyst

E: *formation* of C film on the catalyst surface

F: *diffusion* of C through or around the catalyst particle

G: *incorporation* of C atoms into a growing graphene layer

H: *sputtering* due to ion bombardment

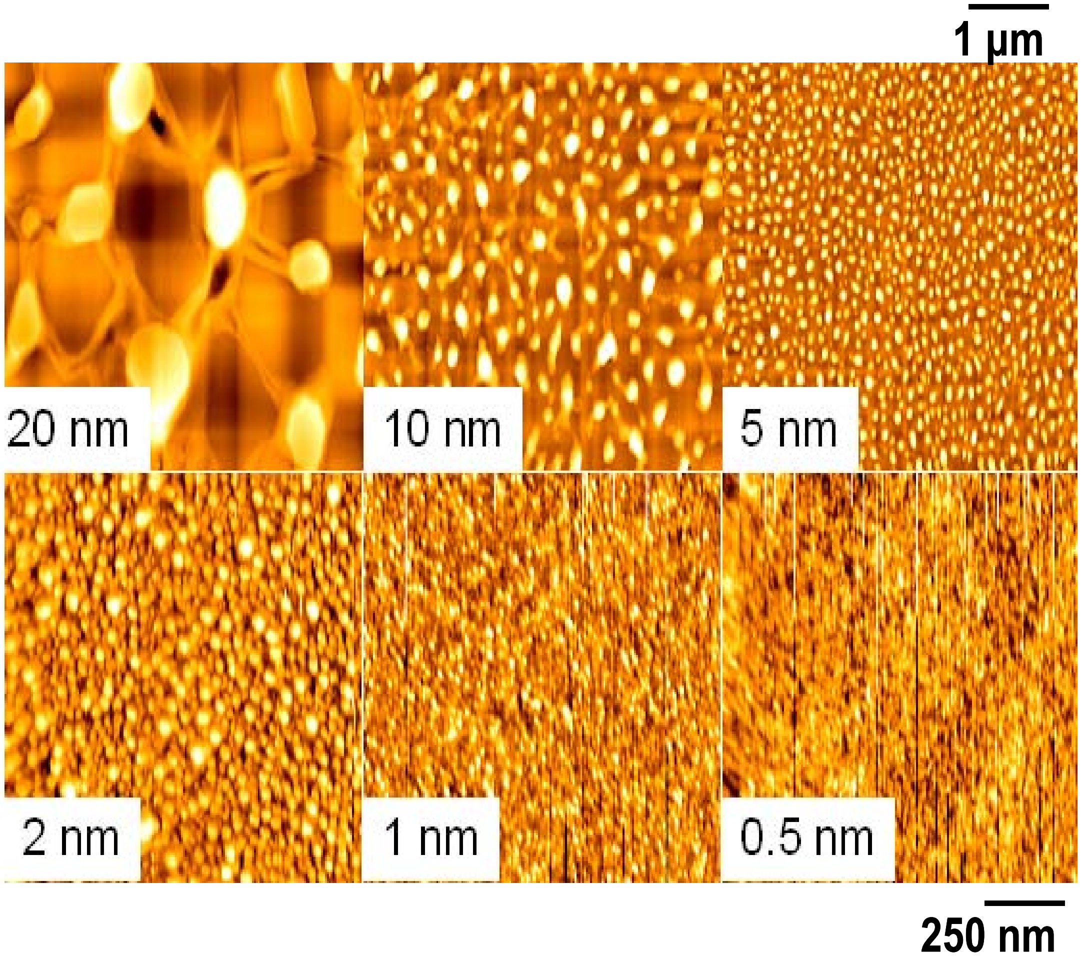
I: chemical *etching* & mechanical force due to interaction of a conducting cylinder with high electric field

Processes at the catalyst nanoparticle in a CVD environment

Variation of Fe island size by changing the initial thickness of Fe film

Results I

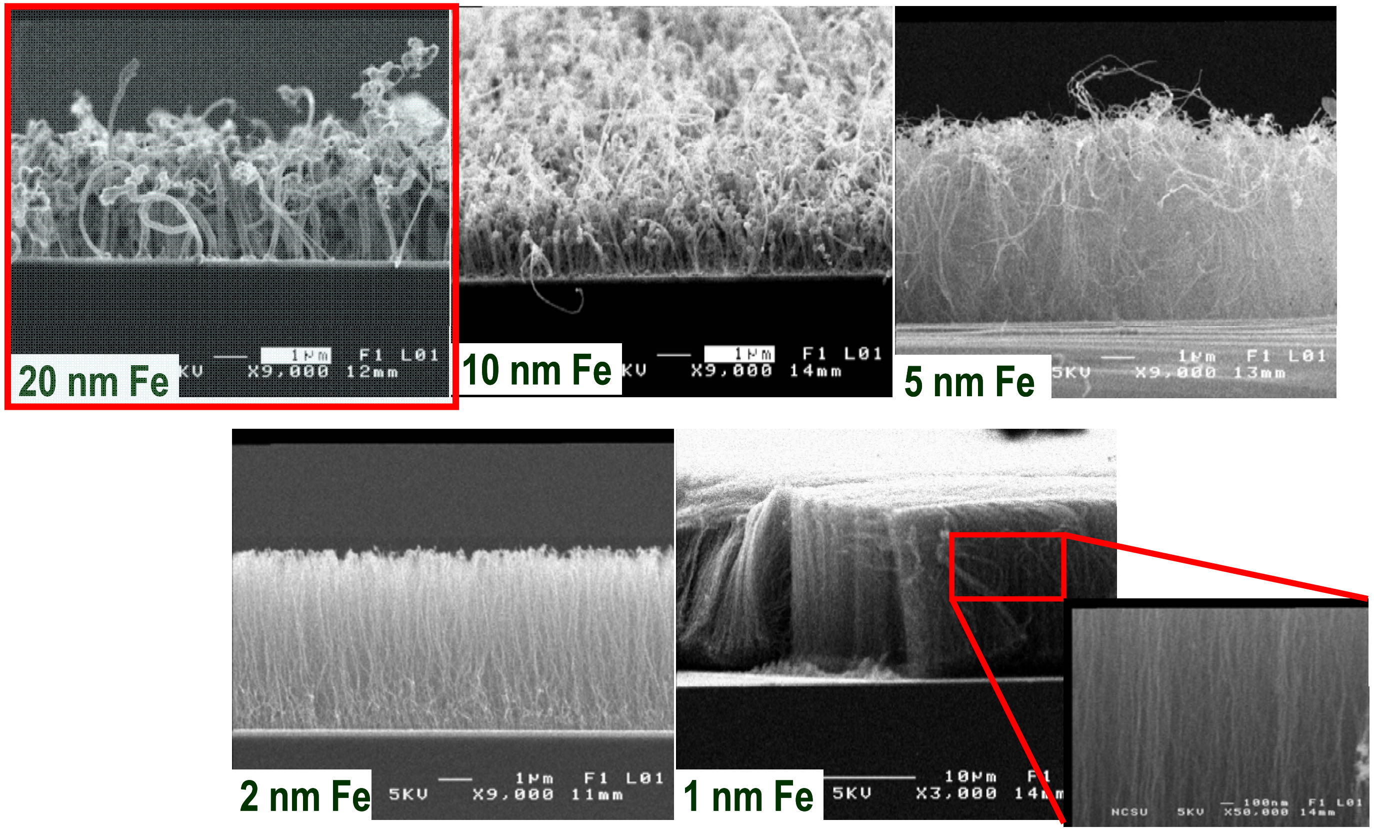
AFM images revealing the topography of annealed (@ 850 ^{o}C for 10 mins) Fe films with different thicknesses



Fe film thickness (nm)	Island size (nm)
20-80	200-600
10	100-200
5	60-120
2	30-60
1	30-50
0.5	10-15
0.3	10-15

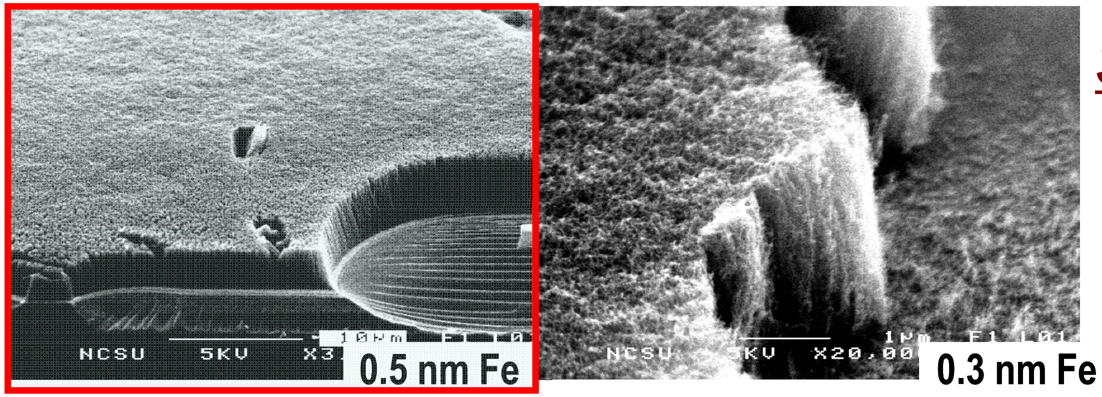
Diameter controlled growth of CNTs by MWCVD

SEM images of vertically aligned CNT films on different thickness of Fe catalyst layer exhibiting an apparent morphological variation

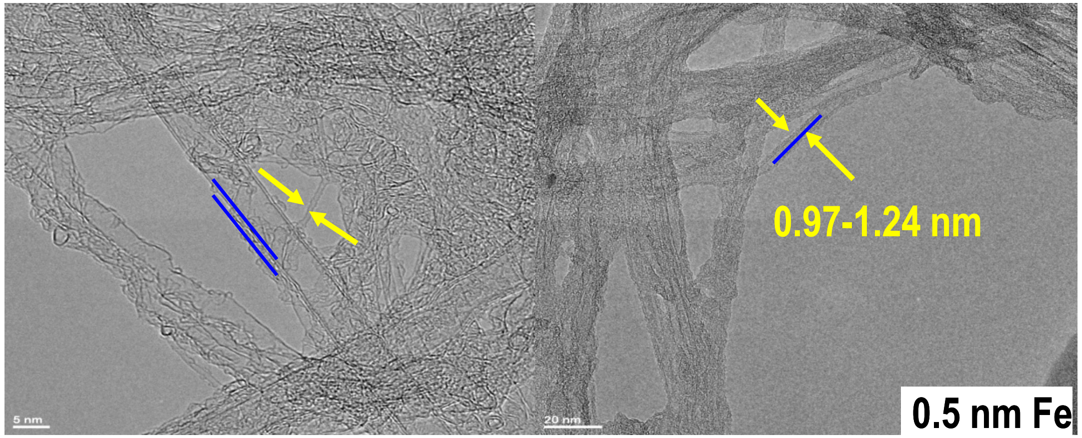


Diameter of nanotubes decreases as Fe film thickness is reduced from 20 to 1 nm. High areal density (~ $10^{13\text{-}14}/cm^2$), less impurity, and better alignment of films are achieved.

HOWEVER, is it possible to grow VA SWNTs ?



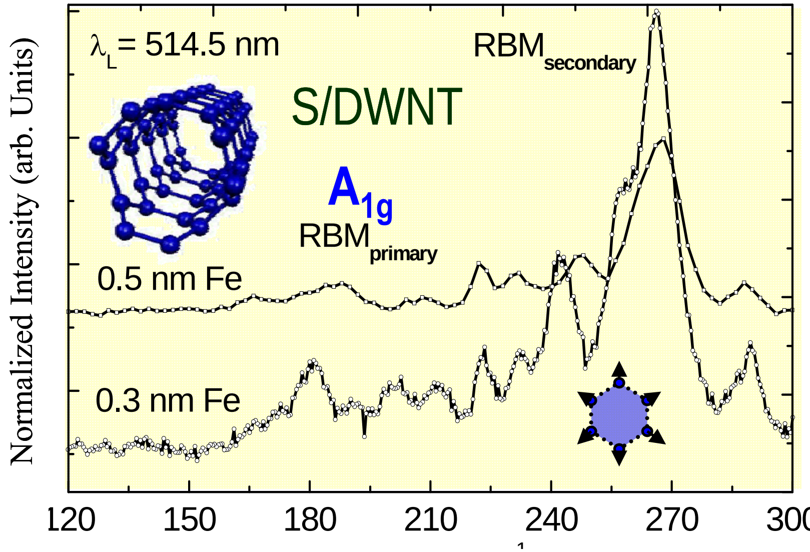
SEM

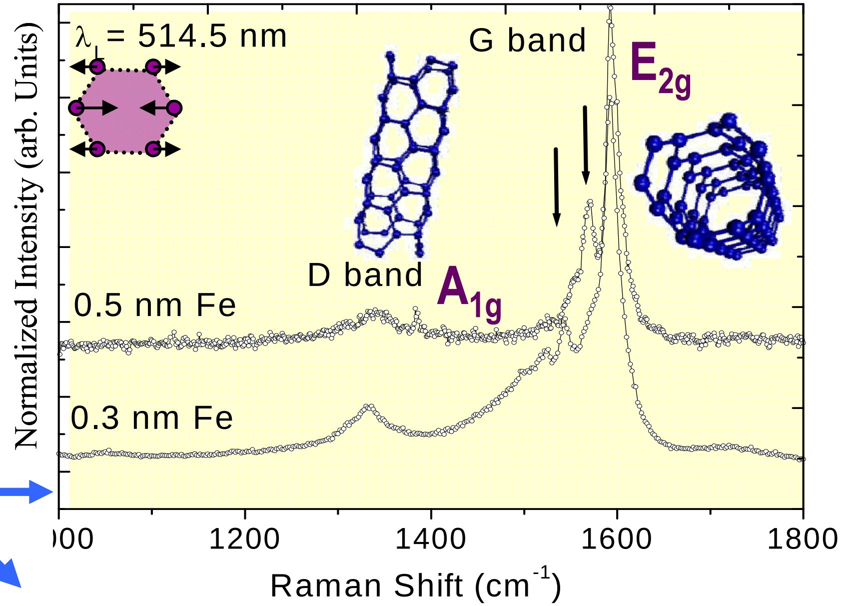


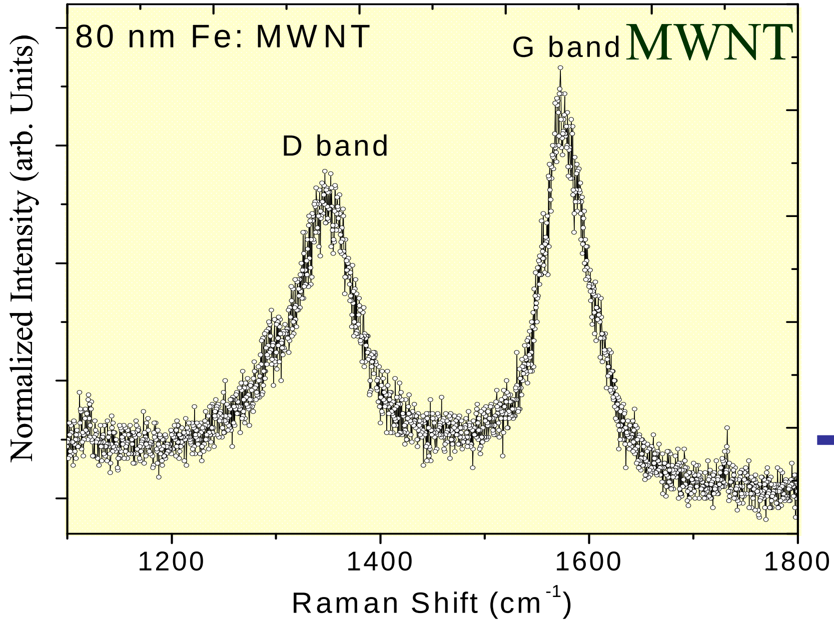
HRTEM

Single- and double walled NTs obtained by continuous reduction of Fe layer thickness (0.3 - 0.5 nm) in conjunction with relative high growth temperature (~ 850 - 900 ° C) and fast growth times (30 - 60 secs).

vis Raman spectra of Single-/double- and multiwall CNT films







$d_t \sim 234/\omega_{RBM}$

0.86 nm (inner) & 1.24 nm (outer)

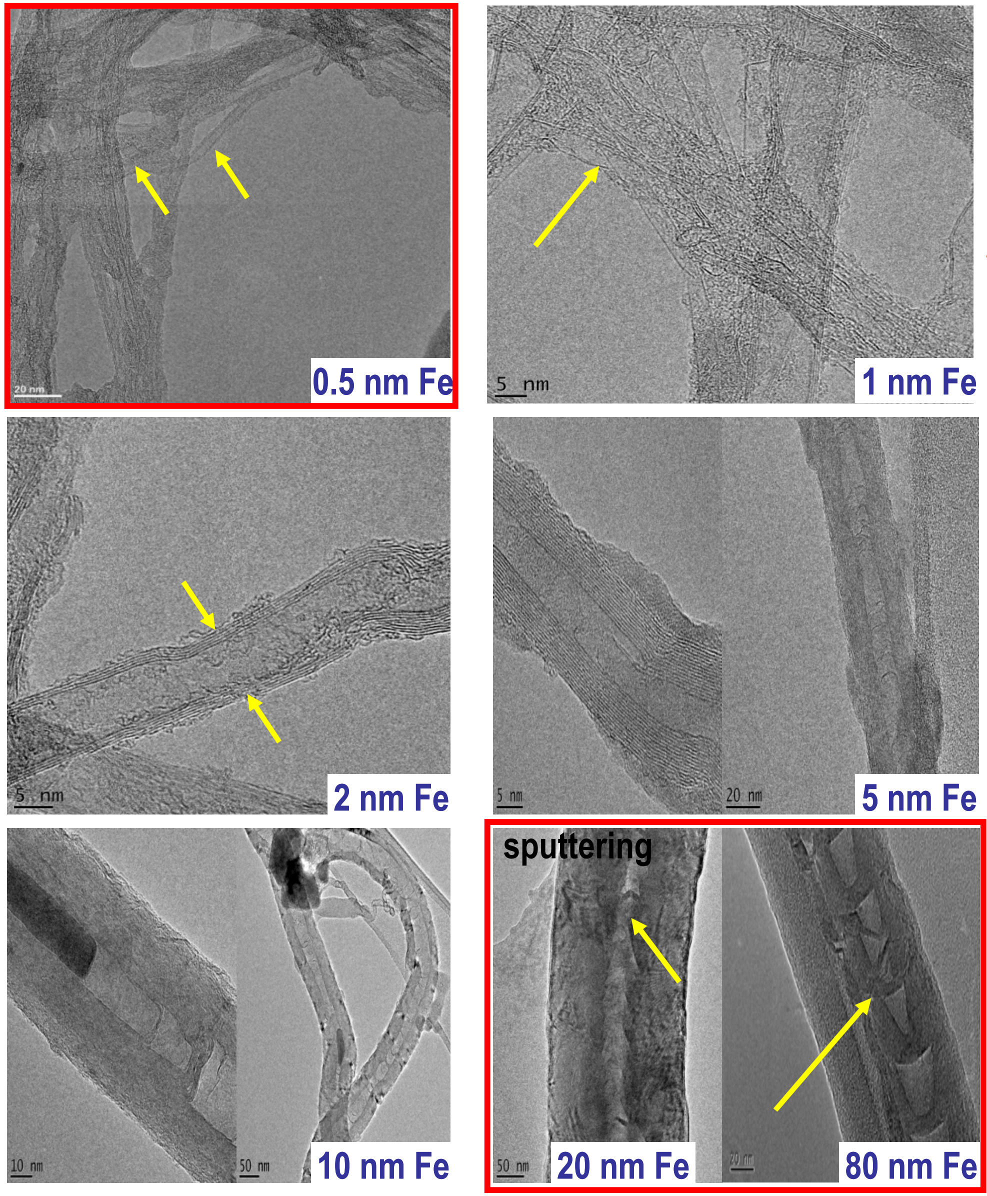
$I_D/I_G \sim 0.12$ (measure of degree of disorder - *purity*)

Invariably absence of RBM and G band splitting in MWNTs unlike $I_D/I_G > 0.8$ SWNTs

Wang, **Gupta** *et. al.* APL **85** (2004) [VJNST]

Internal structural transition of NTs probed using HRTEM: From hollow and bamboo-like to fiber-like

As diameter of nanotubes increases because of increasing Fe layer thickness, the number of tube walls (or shells) increases *i.e.* from single and double to multiwalled. An internal structural transition occurred from hollow- to bamboo-like at Fe thickness of ~ 5 nm.



hollow;

single walled

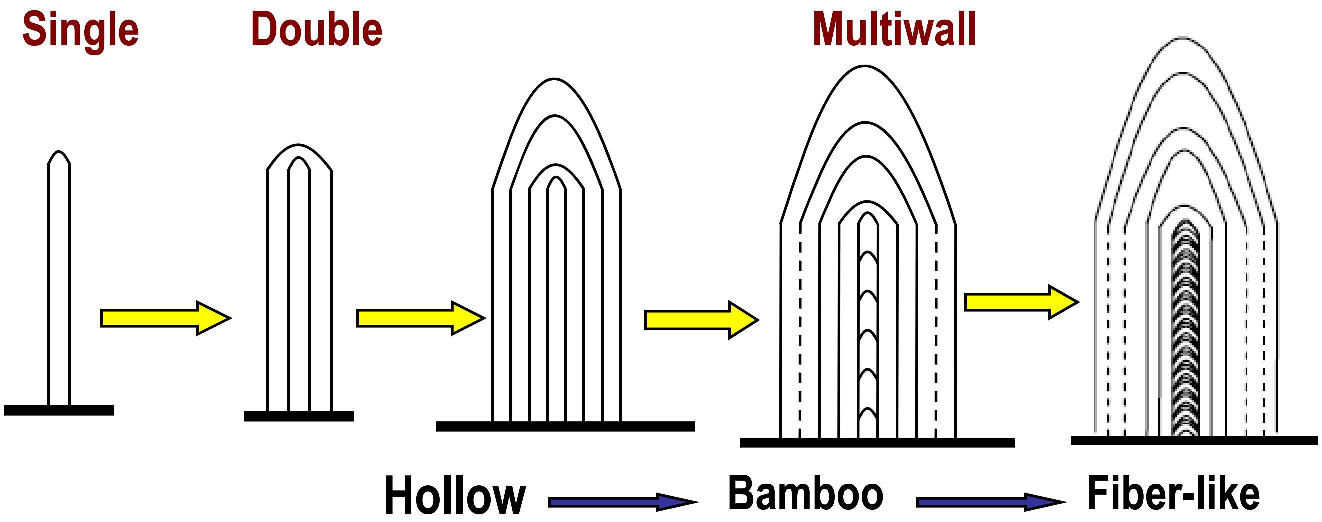
hollow;

multiwalled

0.34 nm

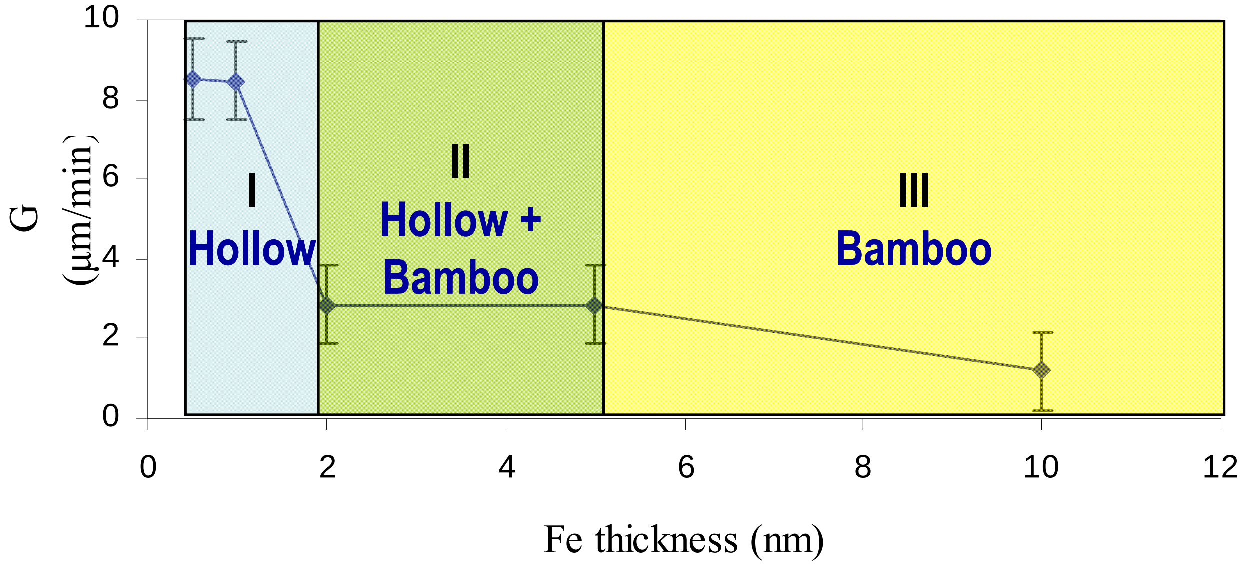
bamboo- &
fiber-like;
multiwalled

Internal structure transition contd…

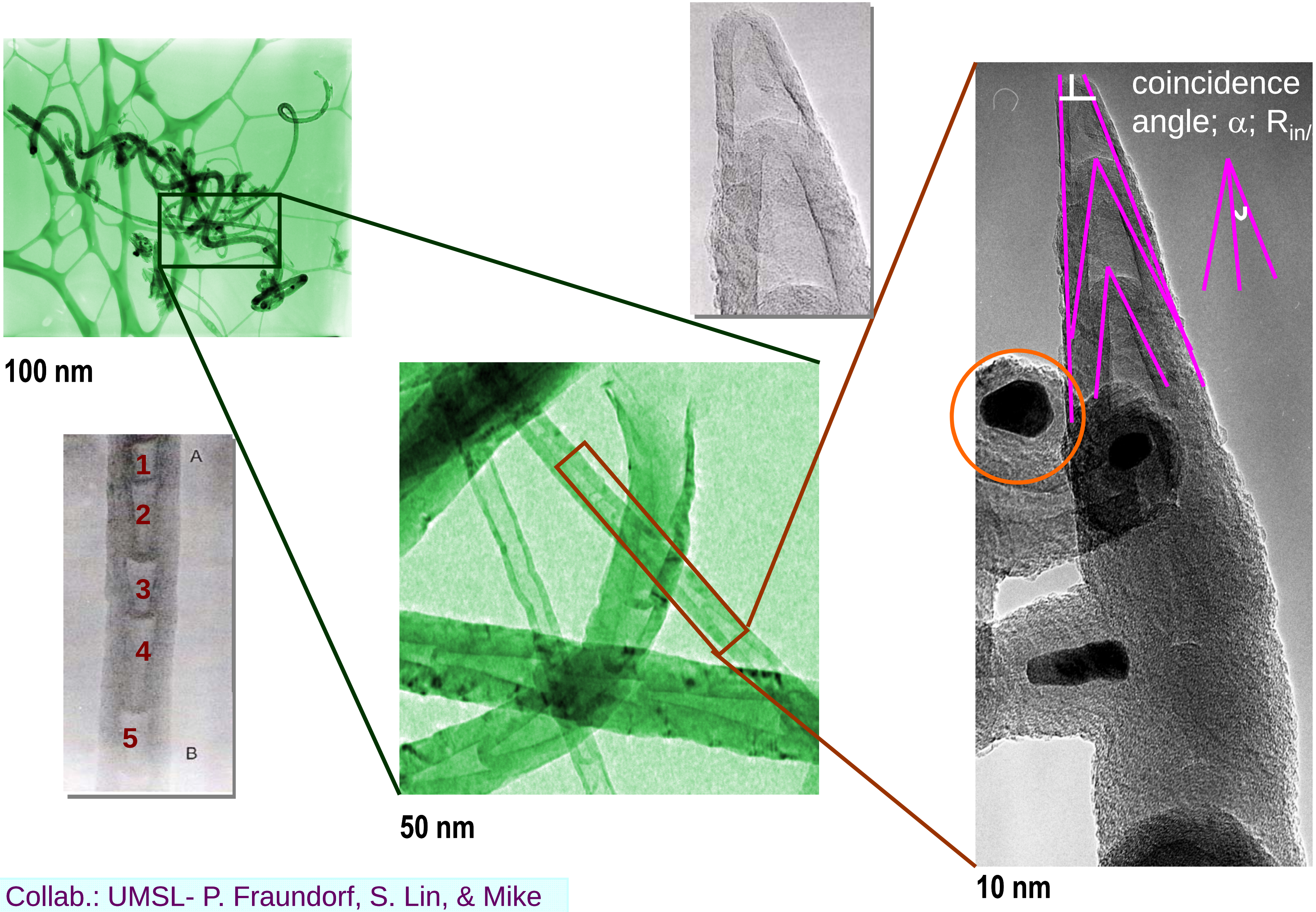


Thermodynamically speaking, surface diffusion is predominant for small size catalyst particles - may be due to large surface to volume ratio - which promotes tube outer wall formation over inter-wall structure resulting in internal structure transition from hollow to bamboo-like.

Variation of Growth rate (μm/min) with Fe layer thickness (nm)



Bamboo-like MWNT HRTEM Images: Chirality and growth mechanism



Collab.: UMSL- P. Fraundorf, S. Lin, & Mike

• <u>All carbon creatures: *Small or big*</u> - *S/DW and MW nanotubes i.e.* diameter controlled VA CNT growth by MWCVD was achieved

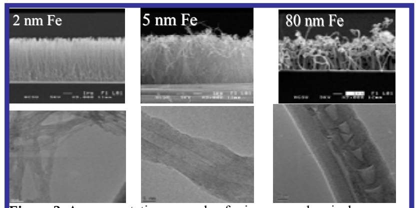
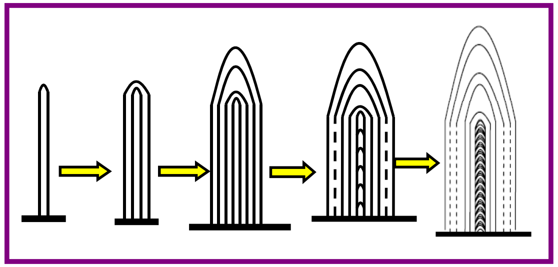
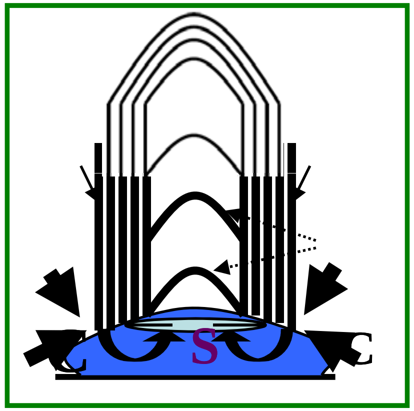


Figure 2. A representative example of microwave chemical vapor deposited (MWCVD) vertically aligned carbon nanotubes images using Fe layer as catalyst [(top) SEM and (bottom) TEM]. Notice that by varying the Fe catalyst thickness from 2 to 80 nm, different kinds of nanotubes can be synthesized *i.e.* from single- and double- to multi-walled and a few-walled in-between.

• <u>Internal structure transition</u> from hollow to bamboo- and fiber-like in NTs was probed as a function of Fe thickness using HRTEM



• Growth model to describe the internal structure transition in terms of <u>surface *versus* bulk</u> diffusion was proposed

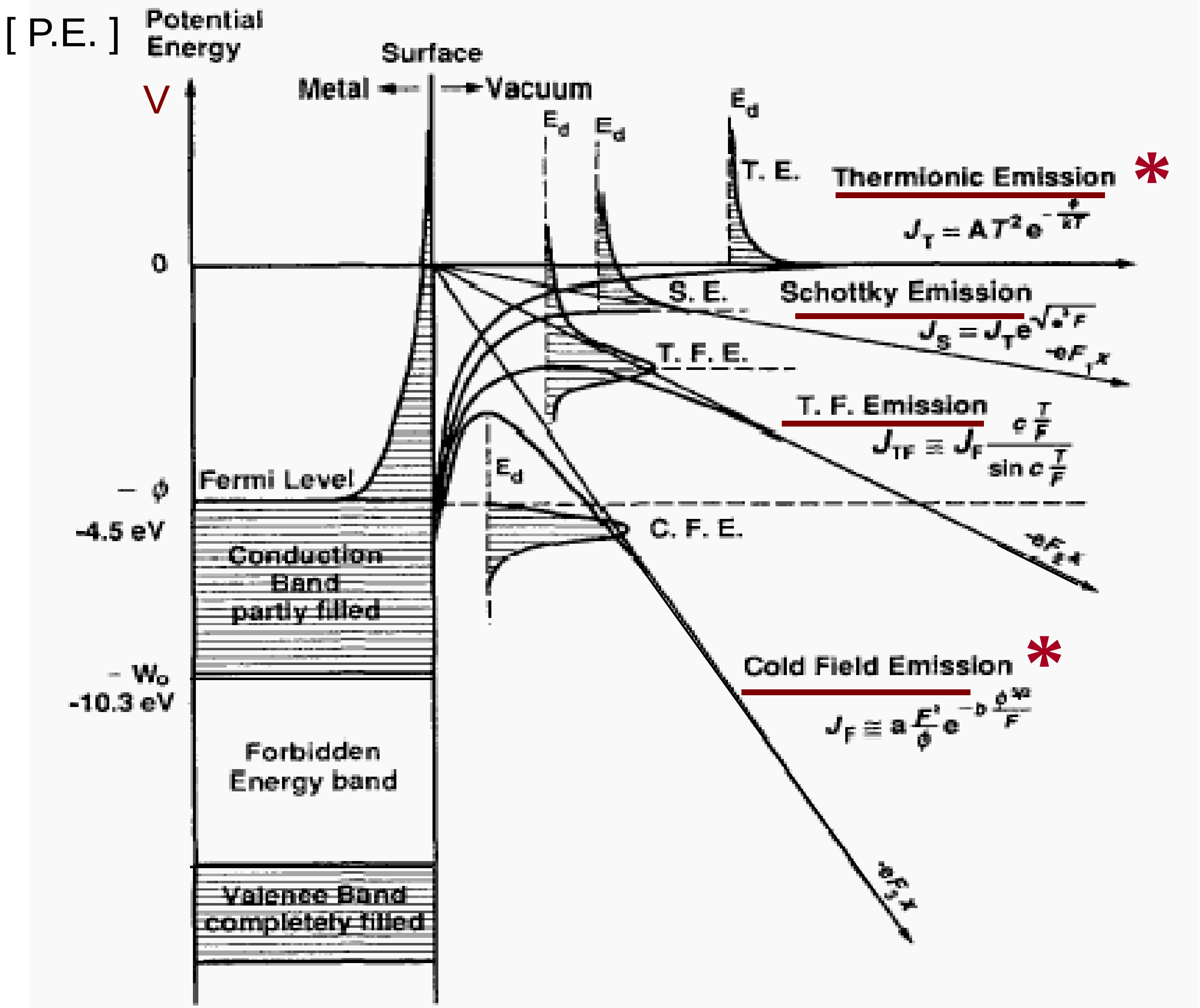


http://materials.ecn.purdue.edu/%7Emdasilva/CNTs.shtml

Comparison of Solid-State and VME Devices

Properties	Solid-State	VME
Current density	10^4-10^5 A/cm^2	~ 2 x 10^3 A/cm^2
Voltage	**> 0.1 kV**	**> 10 V**
Structure	**Solid/Solid interface**	**Solid/Vacuum**
Electron transport		
Medium	Solid	Vacuum
Ballistic	**< 0.1 μm, LT**	**100% Ballistic**
Coherence	**L < 0.1 μm**, t < 10^{-13} s @ RT	**L >> 0.1 μm**, t >> 10^{-13} s
Lens Effect	Difficult	Easy
Noise		
Thermal	Random motion of carriers	Comparable
Flicker	Surface/interface effects	Worse
Shot	Fluctuation in generation/recombination rates of carriers	Comparable
Electron energy	< 0.3 eV	Several to 1000 eV
Cutoff frequency	< 20 GHz (Si) < 100 GHz (GaAs)	< 100-500 GHz
Power	Small	Large
Radiation hardness	Poor	Excellent
Temperature sensitivity	-30 - + 50 °C	< 500 °C
Fabrication/materials	Well established	**Not yet**

Electron Emission Processes



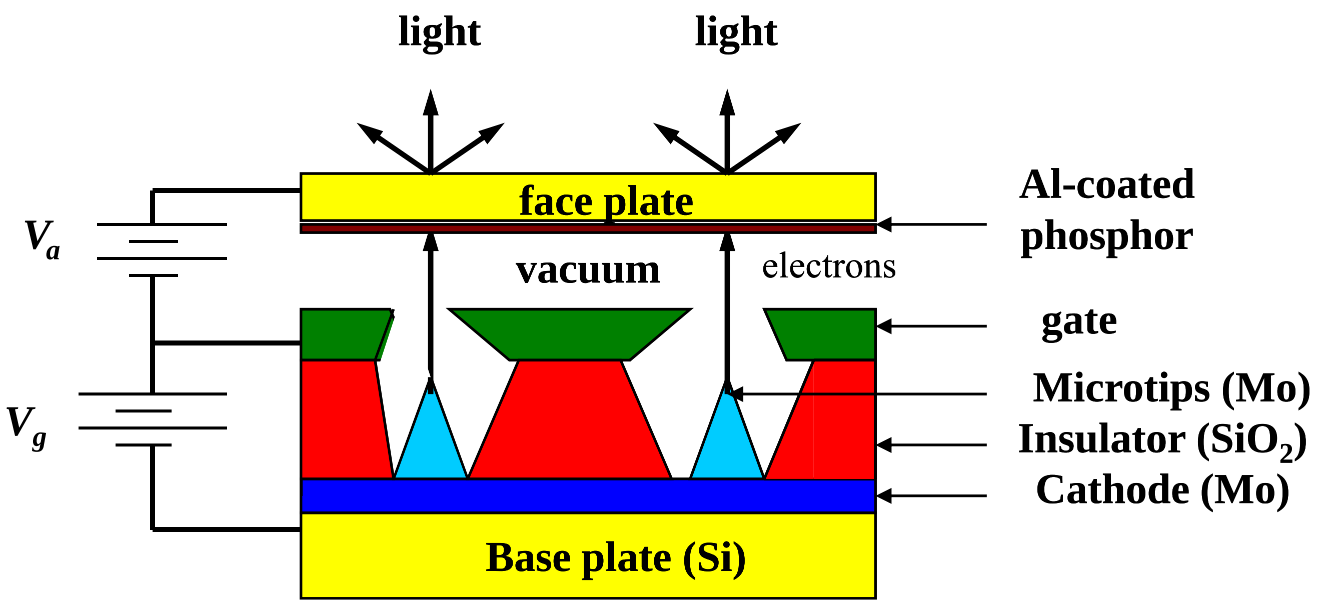
contd…

Thermionic Emission

- Materials: Tungsten, LaB_6
- Low brightness
- High temperature operation (1800 - 2700K)
- Large energy distribution
- Size of source: Macroscopic
- High power required

Field Emission

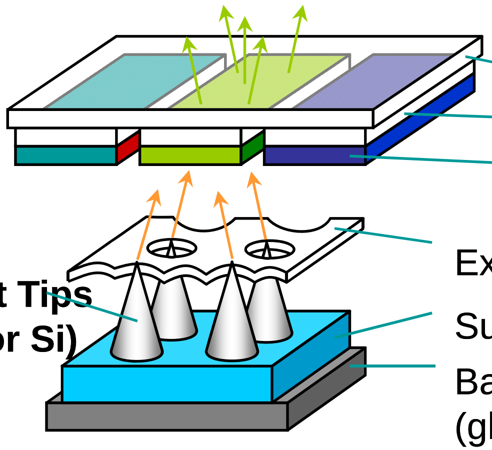
- Materials: Molybdenum, Silicon, Diamond, n-C etc.
- High brightness
- Room temperature operation
- Narrow energy distribution
- Size of source: Microscopic
- High voltage may be required

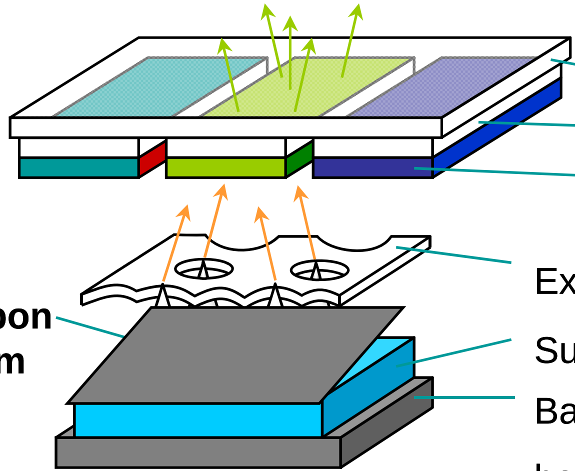


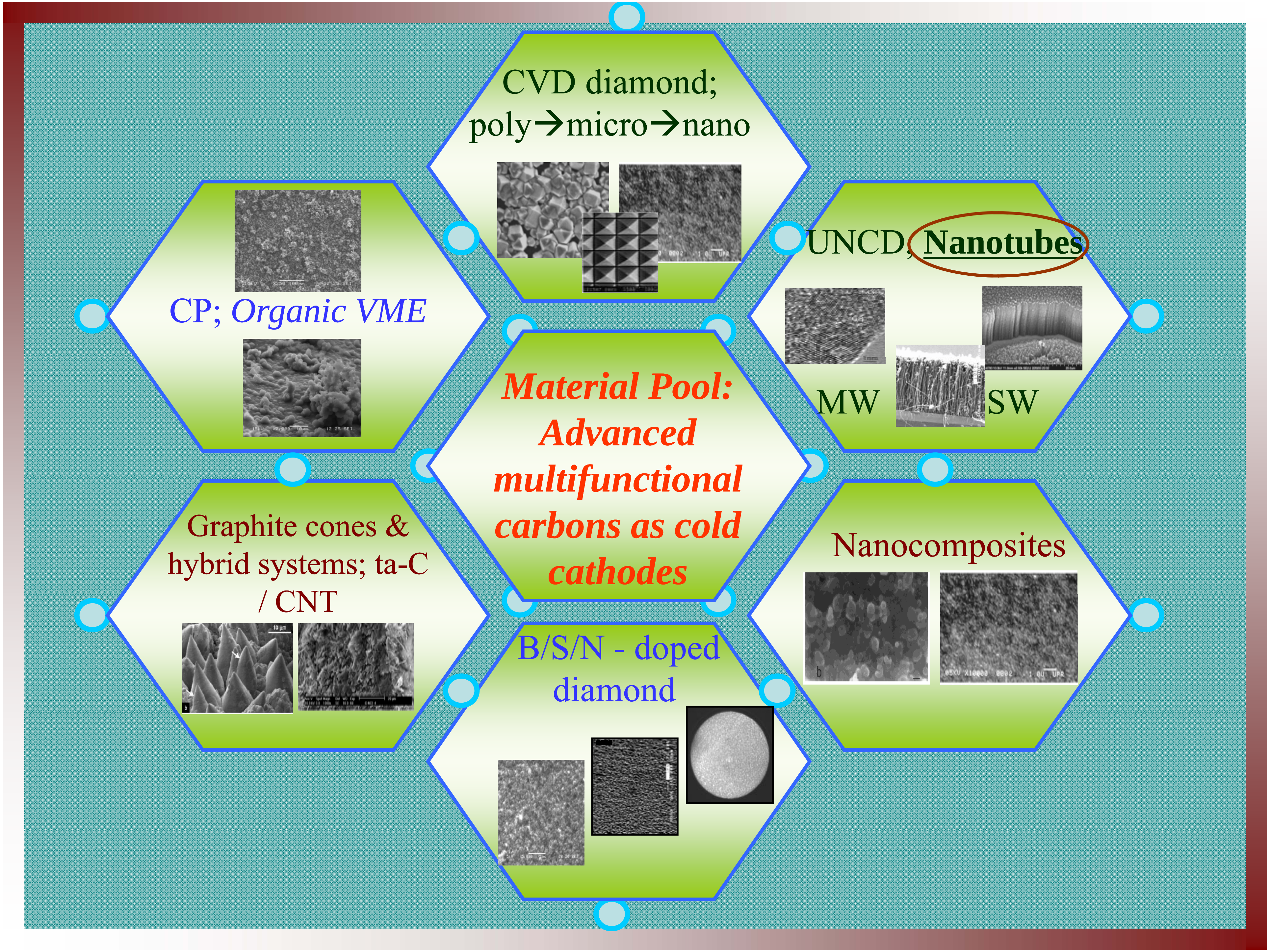
Metal tips: Spindt tips (1976)

Birth of Vacuum Microelectronics (VME)

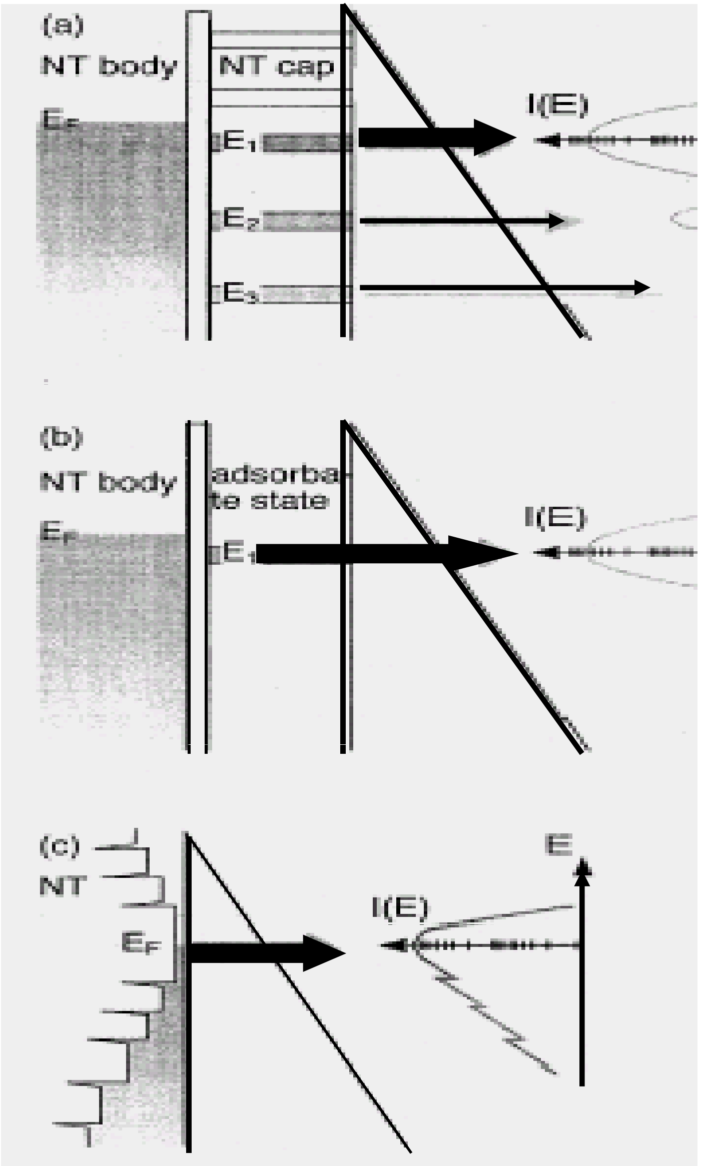
FEDs: A) Spindt tips B) Carbon film cathodes






CVD diamond;
poly→micro→nano
UNCD, Nanotubes
MW
SW
CP; Organic VME
Material Pool: Advanced multifunctional carbons as cold cathodes
Graphite cones & hybrid systems; ta-C / CNT
Nanocomposites
B/S/N - doped diamond

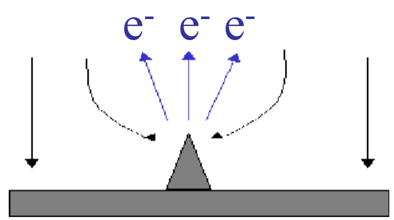
EFE Models: Carbon nanotubes



a) tip enhancement (geometrical)

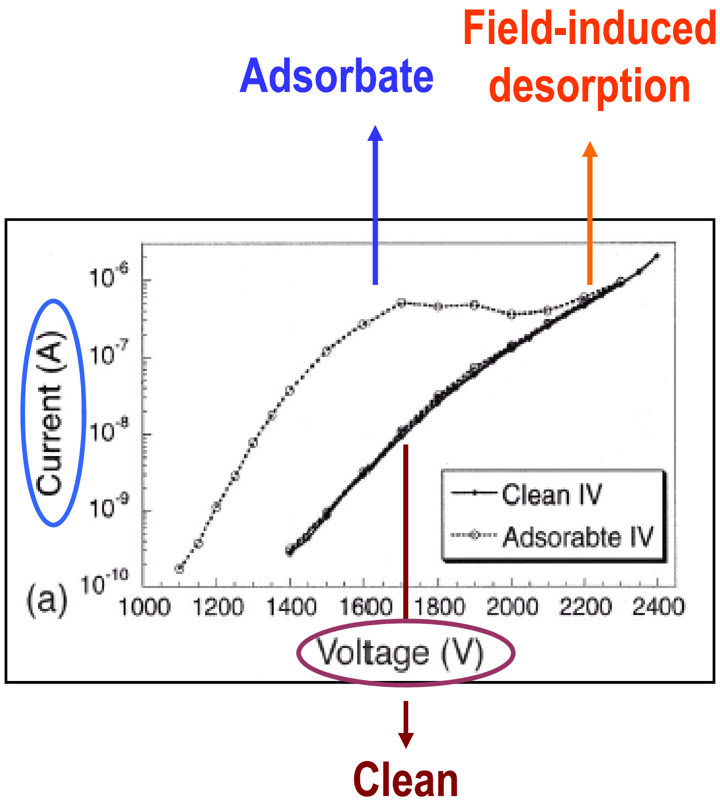
[high aspect ratio structures; β = h/r]

at the tip



b) adsorbate resonant tunneling

c) metallic SWNT DOS

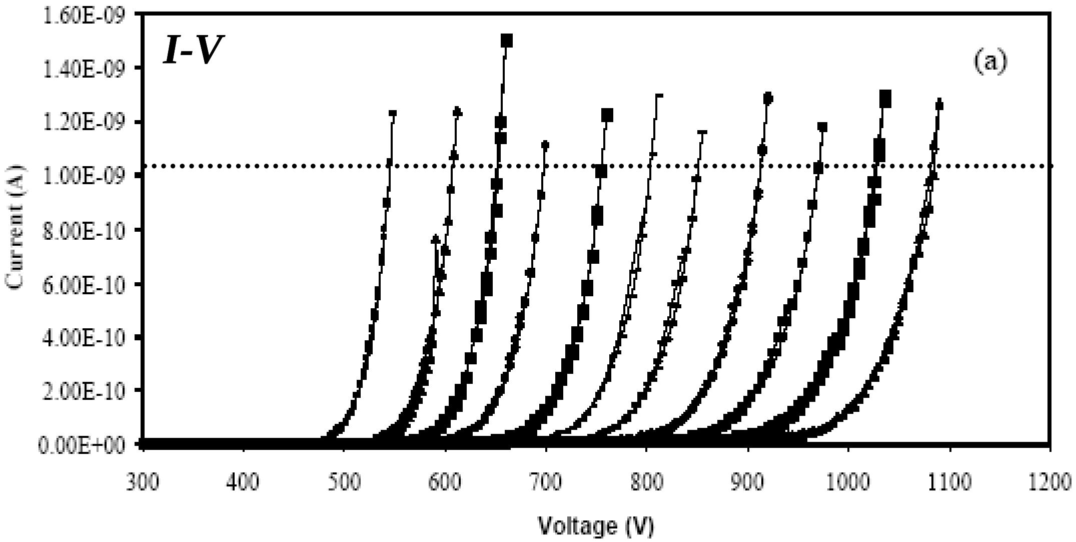


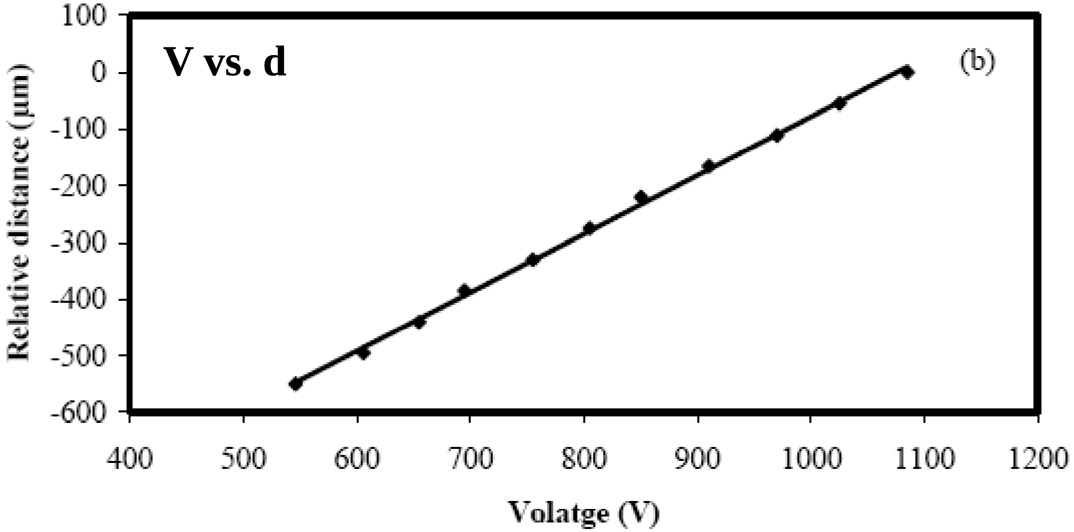
Bonard, SSE (2001).

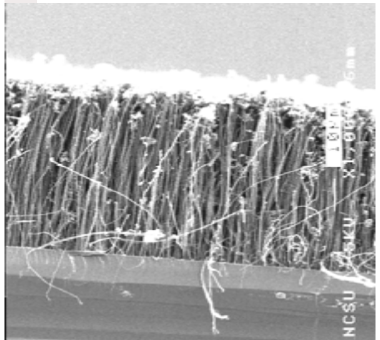
I-V characteristics and Imaging: Single- *versus* multiwalled nanotubes

Results II

Field Emission Results: MW nanotubes

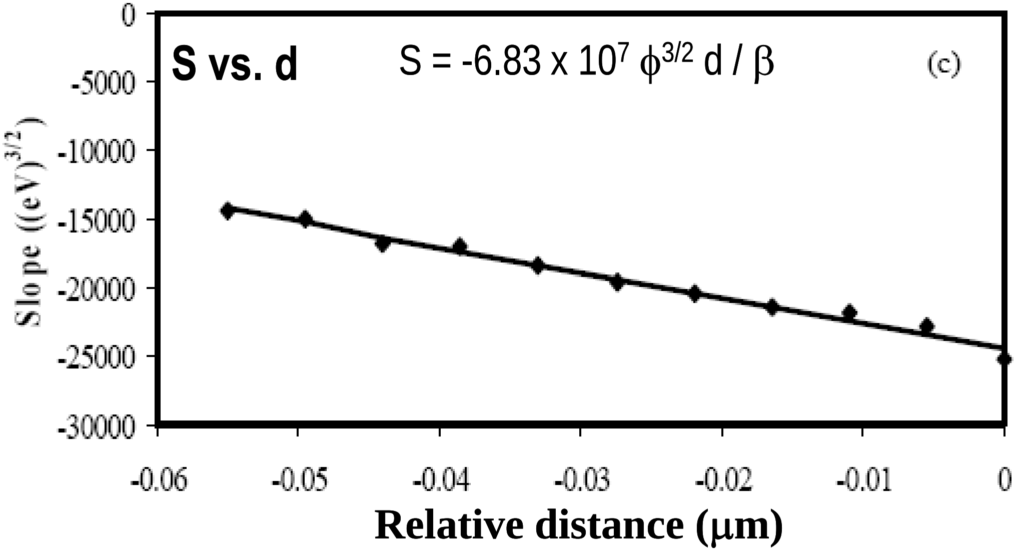


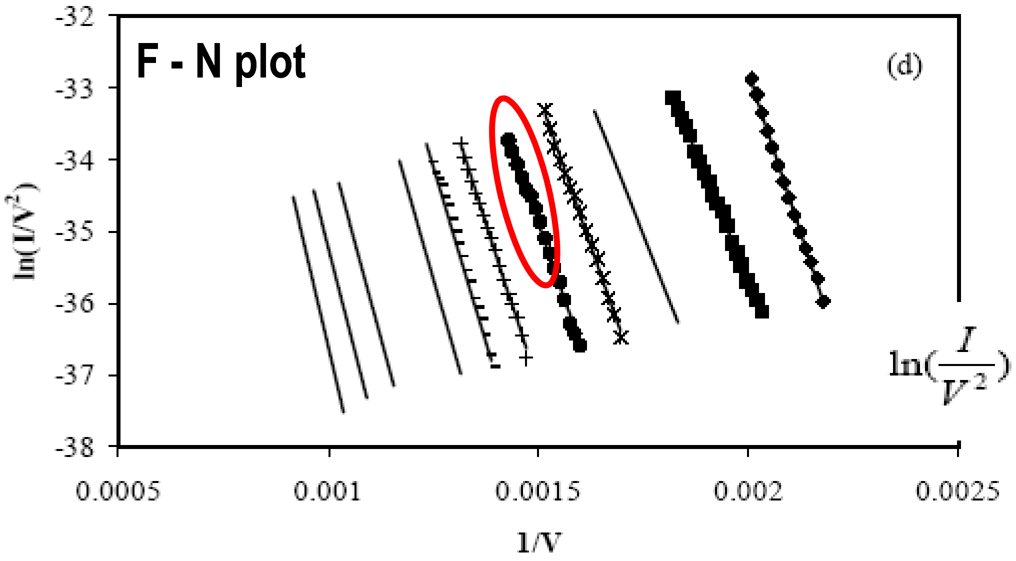




80 nm Fe

Field Emission contd…





$$\ln\left(\frac{I}{V^2}\right) = a - \frac{S}{V}$$

Slope = -1.84 x 10^5 $(eV)^{3/2}$

ϕ= 5.0 eV

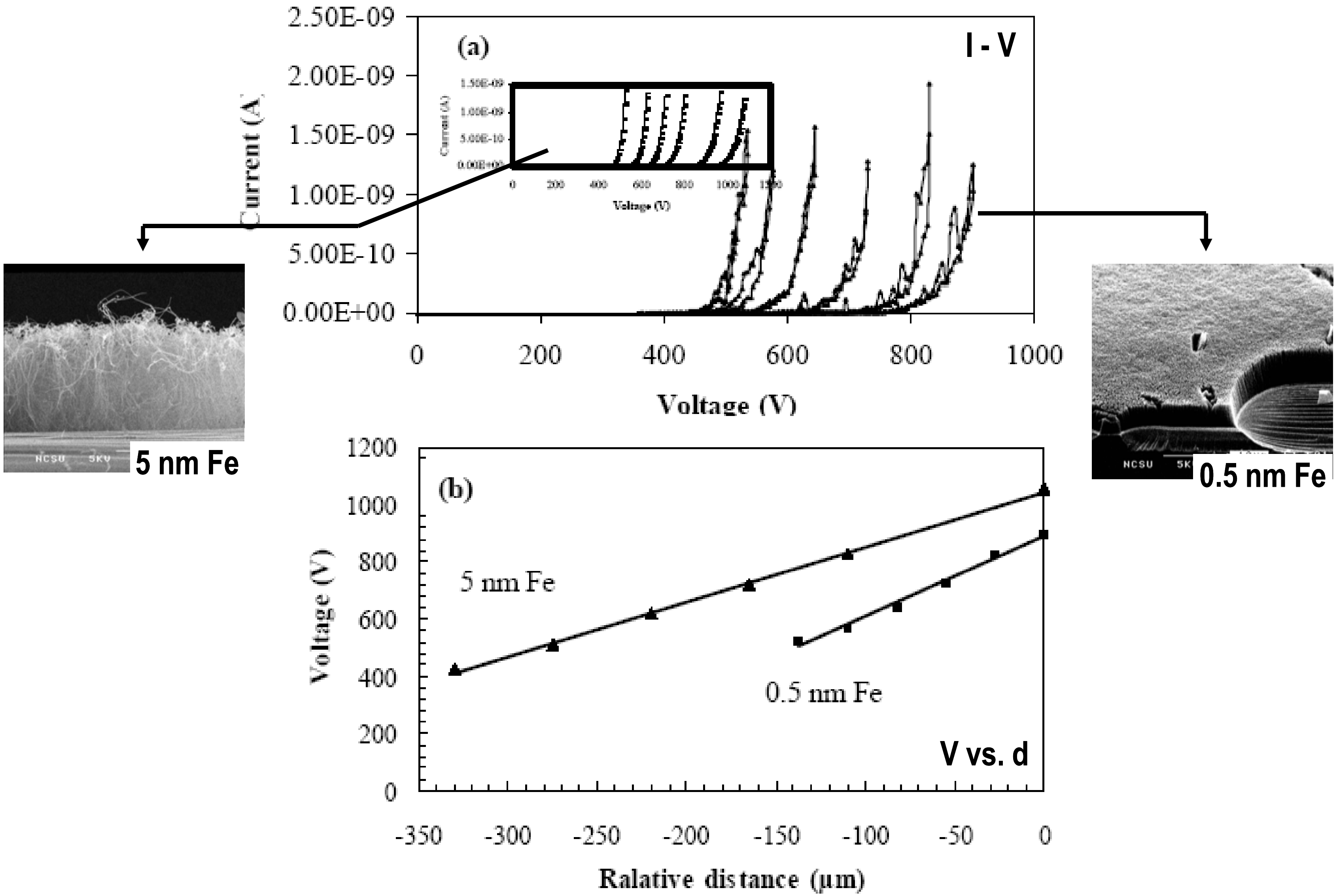
β = 4140

E_{thr}: ~ 1 V/μm

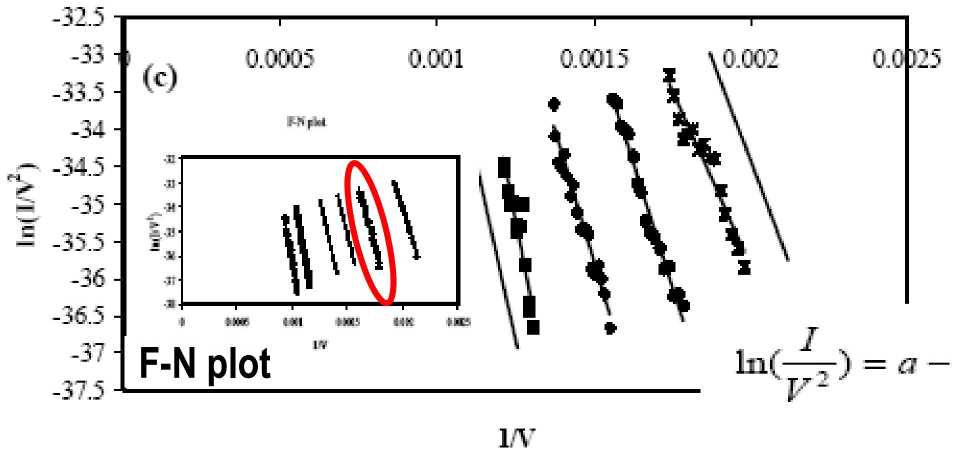
V_{max} = -3.79 $E^{1/2}$ eV

(lowering barrier by almost 2.4 eV)

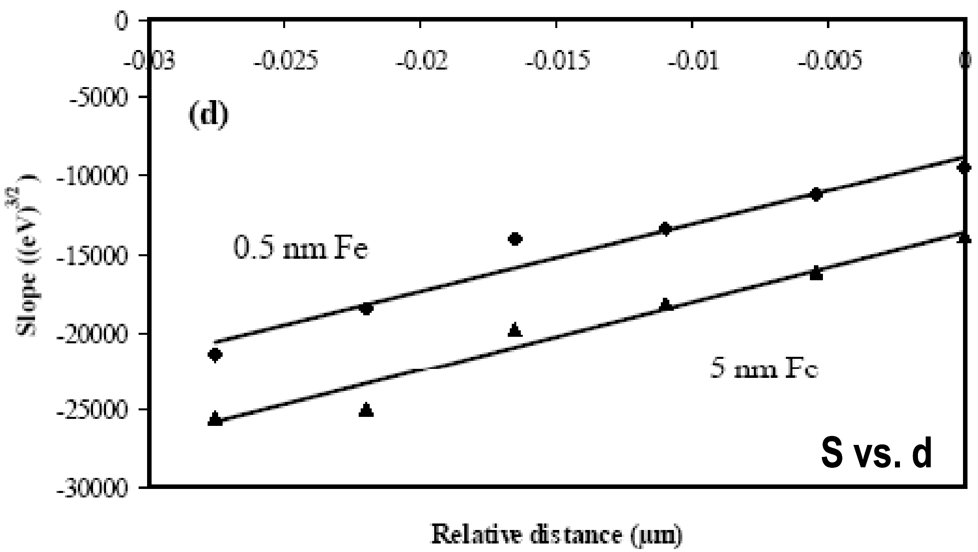
Field Emission Results: S/DW nanotubes



Field Emission Results: S/DW nanotubes



$$\ln\left(\frac{I}{V^2}\right) = a - \frac{S}{V}$$



Slope (S) = -1.84×10^5 $(eV)^{3/2}$

ϕ = 5.0 eV

β = 1700

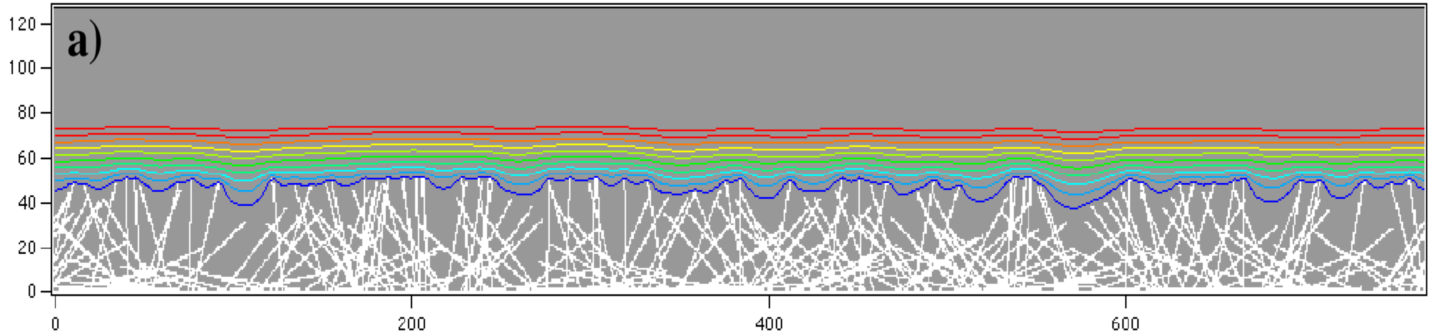
E_{thr}: ~ 2 - 5 V/μm

$V_{max} = -3.79\, E^{1/2}$ eV

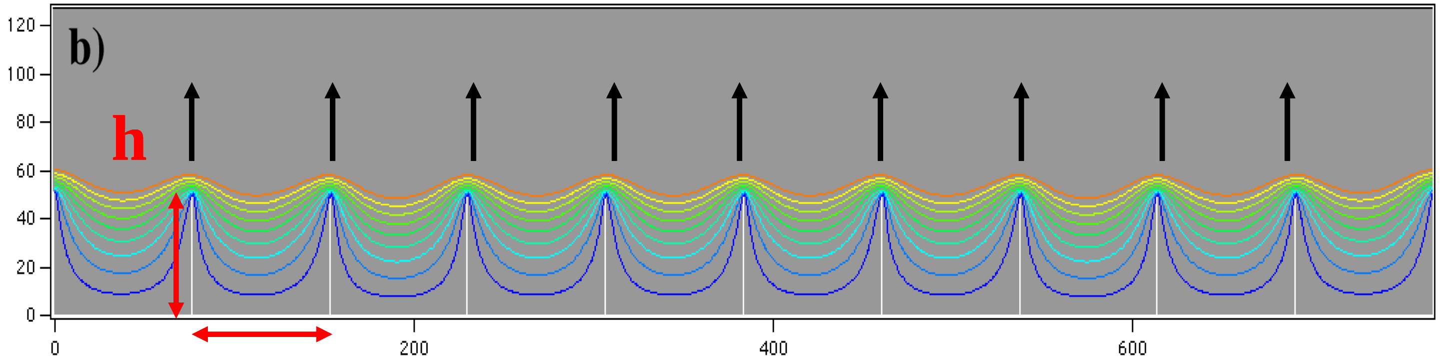
(lowering barrier by almost 2.6 eV)

(for both 0.5 and 5 nm Fe films)

Discussion: Simulation of electric field distribution: CNTs



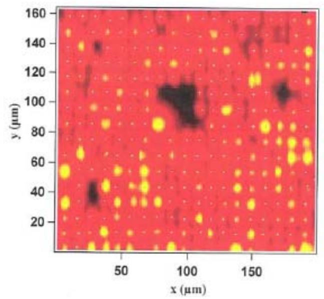
a) densely packed random arrangement of nanotubes



b) regularly spaced single nanotubes

d > h

$$N(F) = N_0 \exp(-b/F)$$
$$\sim N(\beta) = N_0 \exp(-\beta/\beta_0)$$



Distribution of beta

Robertson *et. al.* JVST A (2000).

Thesis Minoux, Thales 2006 : O.Groening,

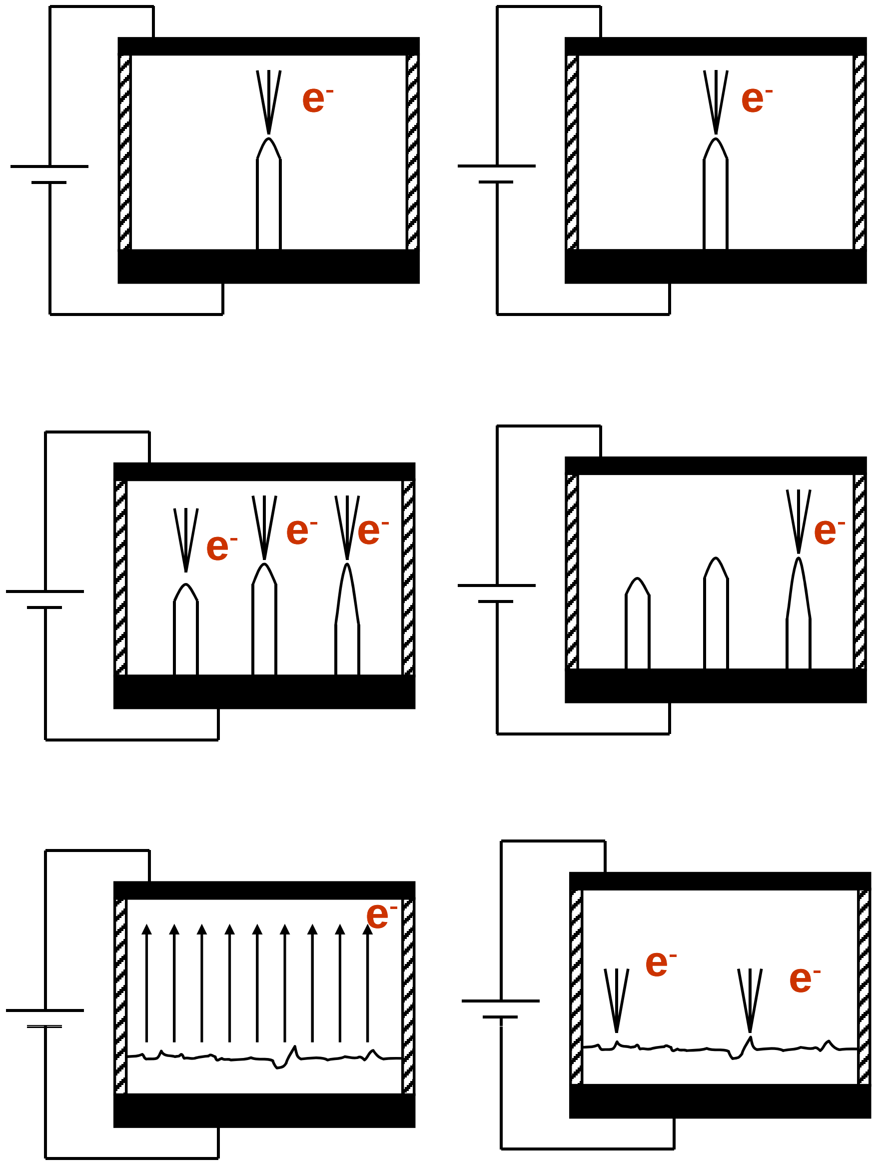
Parallel-Plate Field Emission Measurements

Wishful Thinking *Reality*

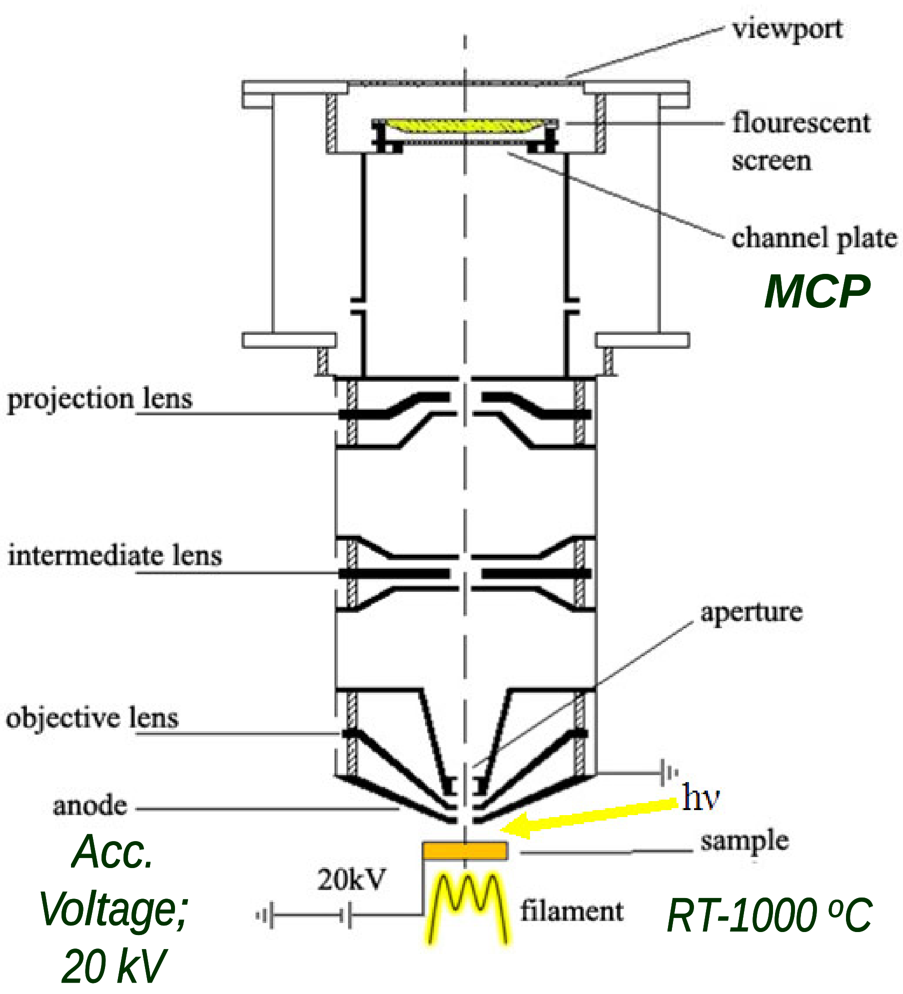
Single Tip

Array of Tips

Thin Film



Detecting Electron Emission: Electron Emission Microscopy



Modes of operation:

Photo Electron Emission Microscopy *(PEEM)*

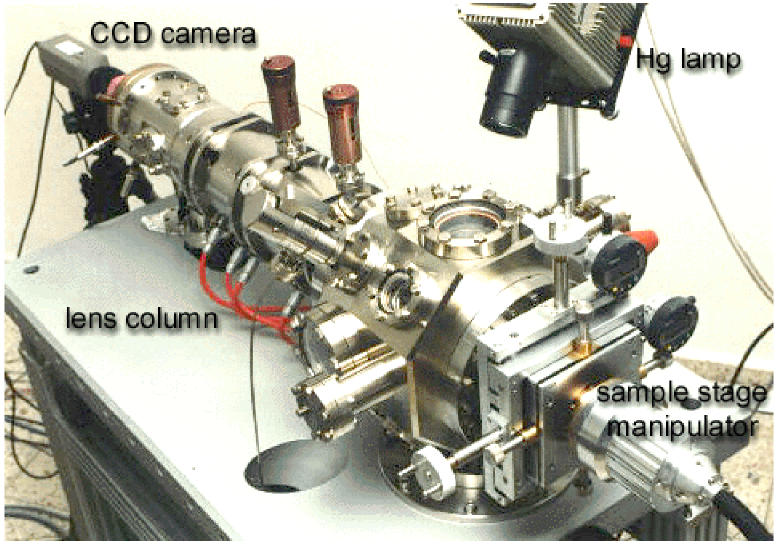
Excitation with UV light source

* **Field** Electron Emission Microscopy *(FEEM)*

Turn off the UV light source

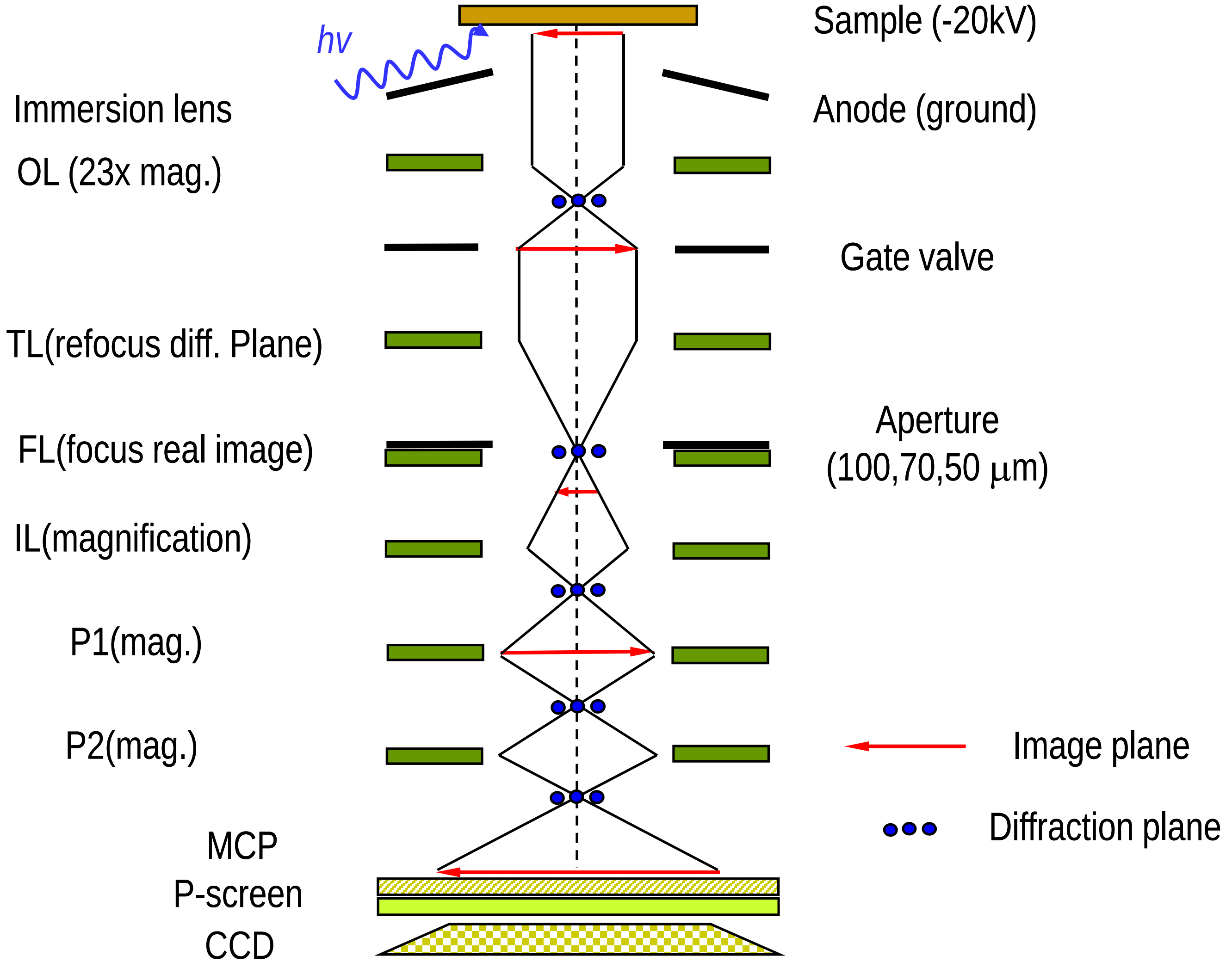
* **Thermionic Field** Electron Emission Microscopy *(T-FEEM)*

Temperature dependence (no light source)



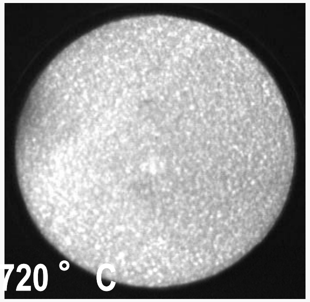
NCSU + Duke
OK-4 FEL

PEEM Lens column



Comparison of electron emission: nano-engineered cold cathodes

N-doped Diamond

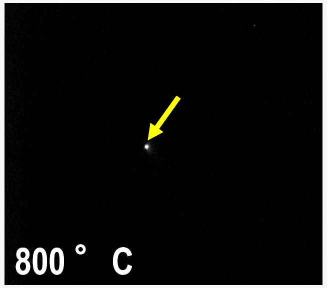


150 μm FoV

- Uniform emission
- Temperature dependence
- NEA surface
- Spatial connectivity

Background

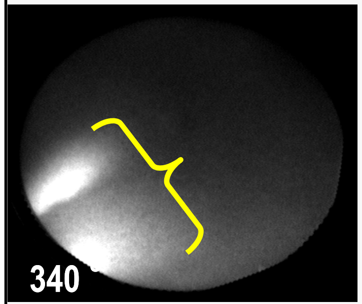
Undoped nanocrys-talline diamond



150 μm FoV

- Non-uniform emission
- Weak temperature dependence -
- Field enhancement
- Electronic states
- weak spatial connectivity

S-doped nanocrys-talline diamond

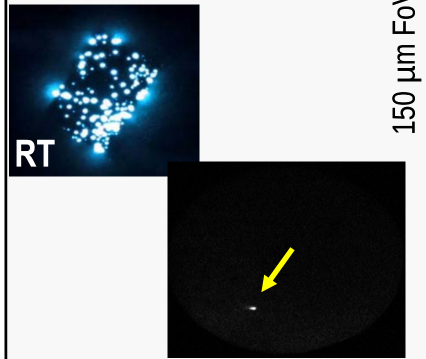


C

150 μm FoV.

- Non-uniform emission (localized)
- Temperature dependence + Field enhancement
- S-related states electronic states
- Spatial connectivity
- low temperature thermionic emitters & thermionic energy converters

Vertically aligned Carbon Nanotubes



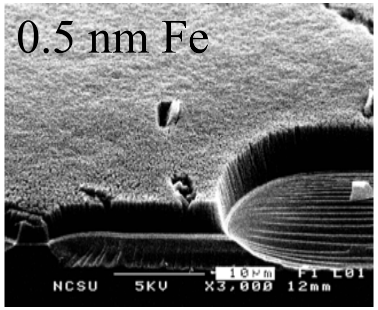
150 μm FoV

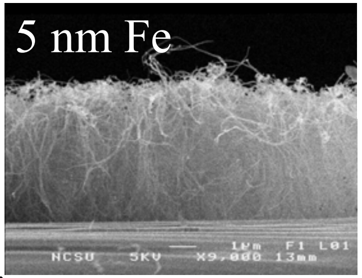
- Non-uniform emission
- Temperature dependence + adsorbates
- Intrinsic behavior (geometrical)
- low temperature thermionic emitters & thermionic energy converters

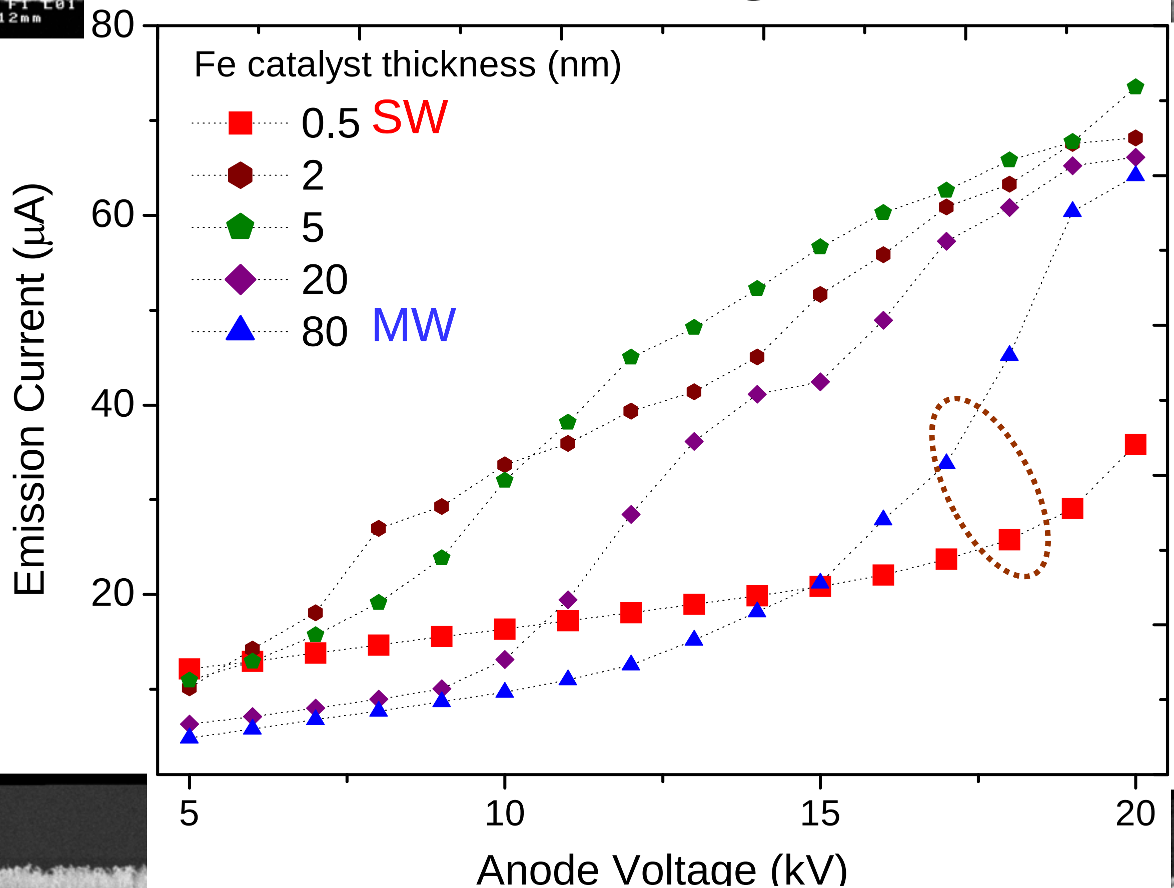
Gupta et. al. DRM (2004).
Gupta et. al. DRM (2005).

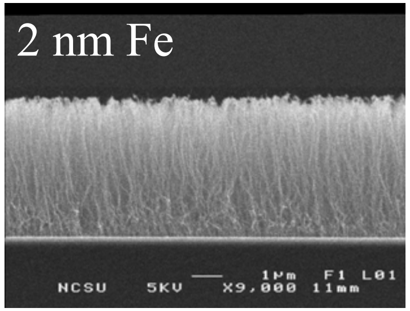
Nanotube diameter dependent electron field emission

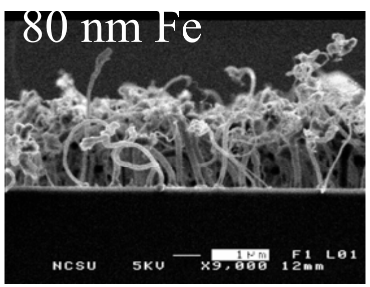
I - V curves @ RT





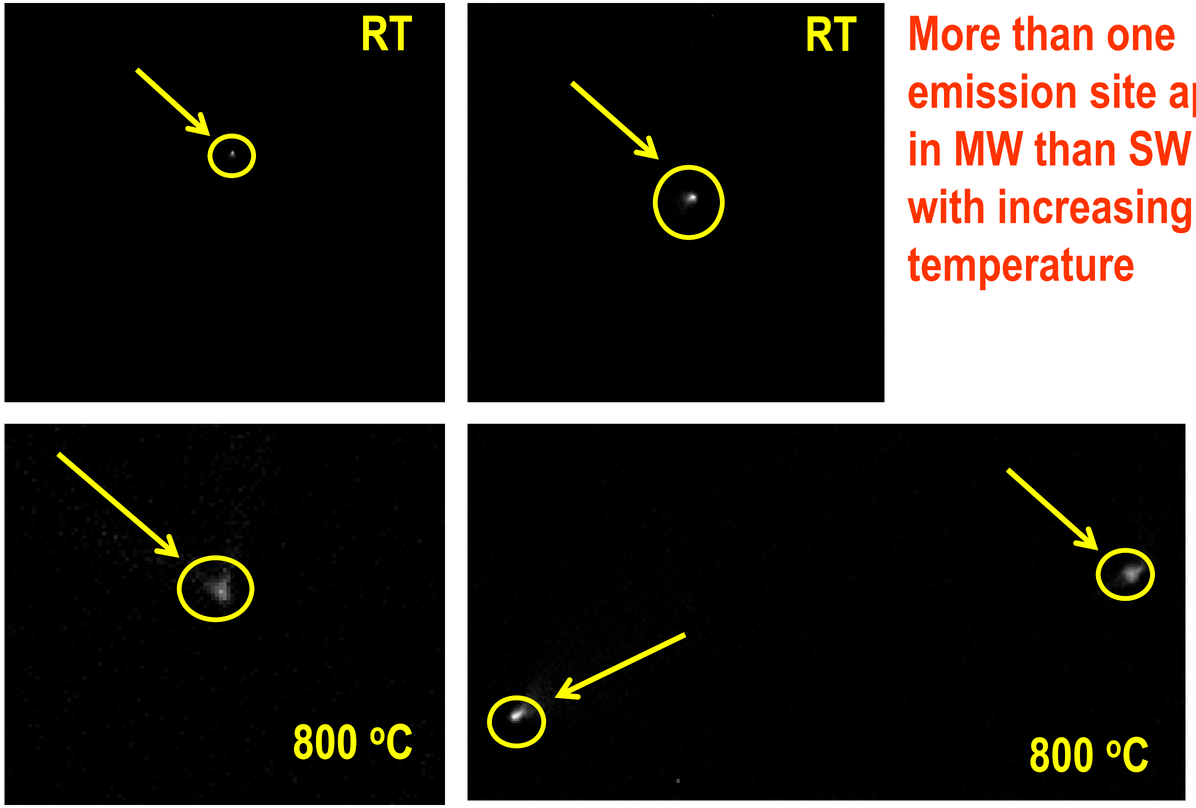






Thermionic dependent electron emission imaging: A comparison

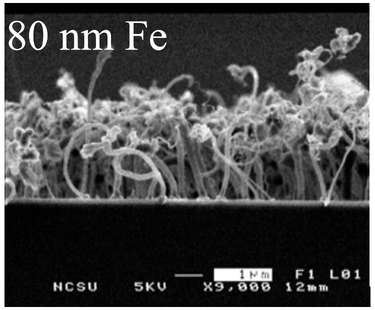
SW *versus* MW Nanotubes

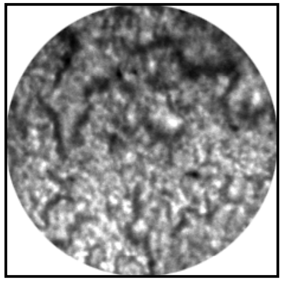


More than one emission site appear in MW than SW NTs with increasing temperature

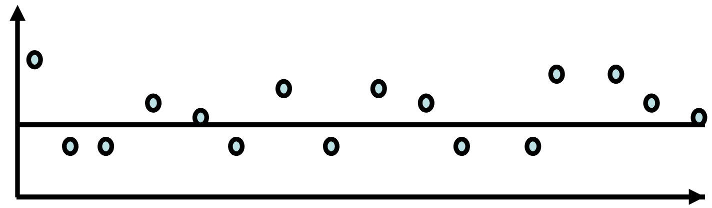
Emission Intensity Fluctuation - Flicker Phenomenon

I. MW carbon nanotubes

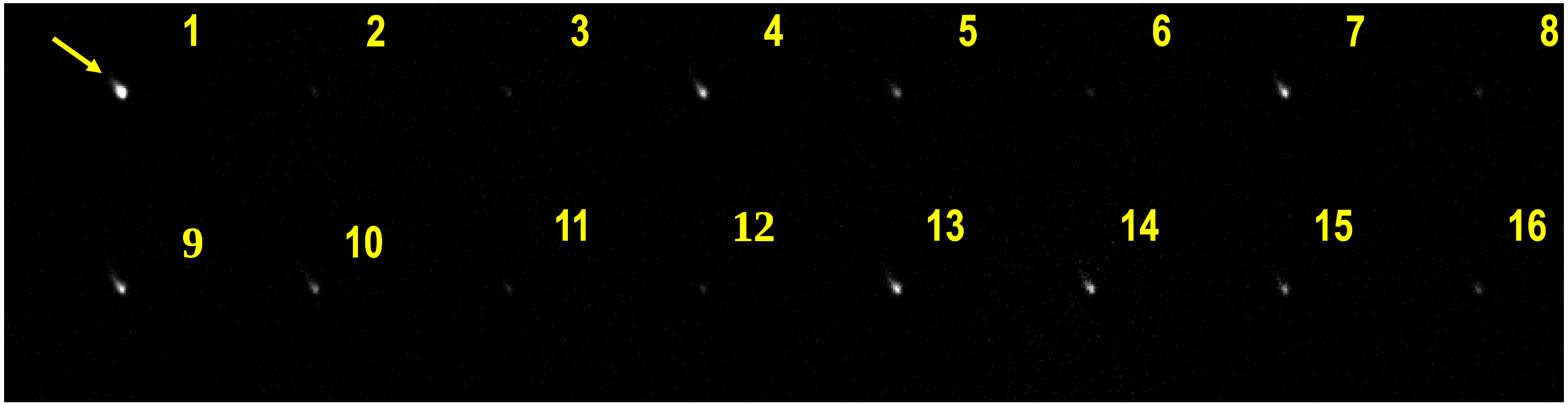




PEEM

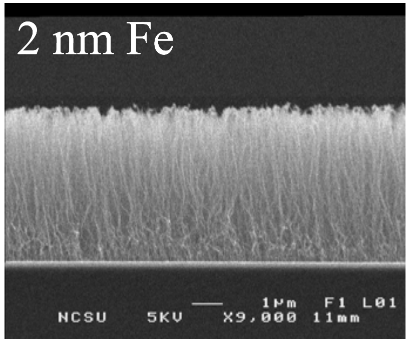


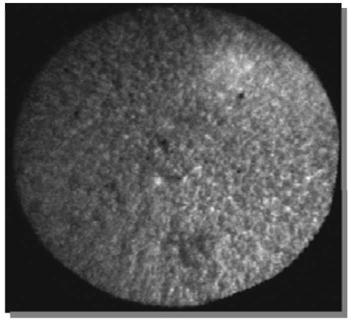
CNT film on 80 nm Fe catalyst layer

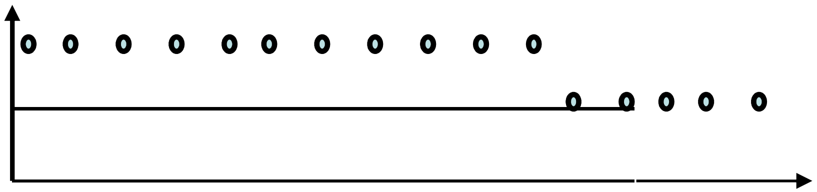


1.10 kV MCP, 1.4 x 10^{-8} Torr, 50 μm FoV (clipped from 150 μm)
Microscopy snapshots @ 100 °C

II. SW carbon nanotubes

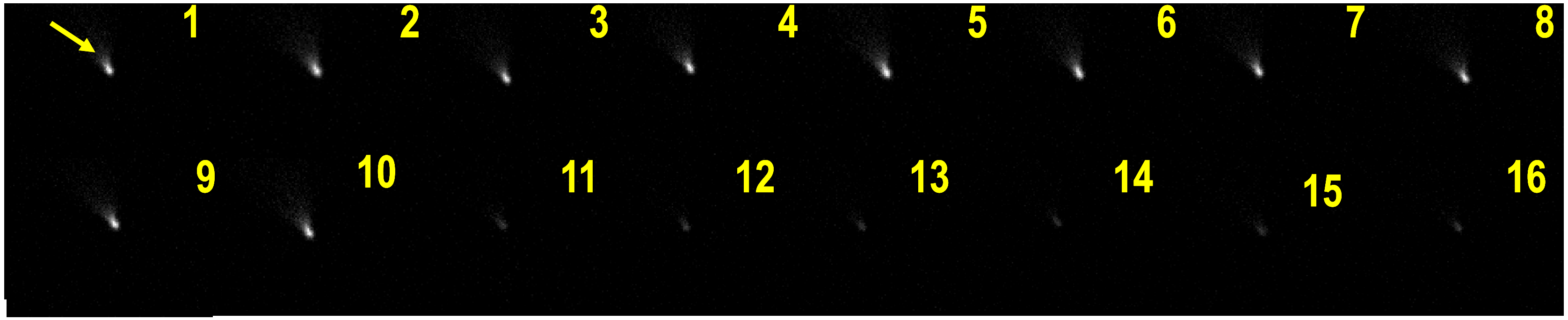




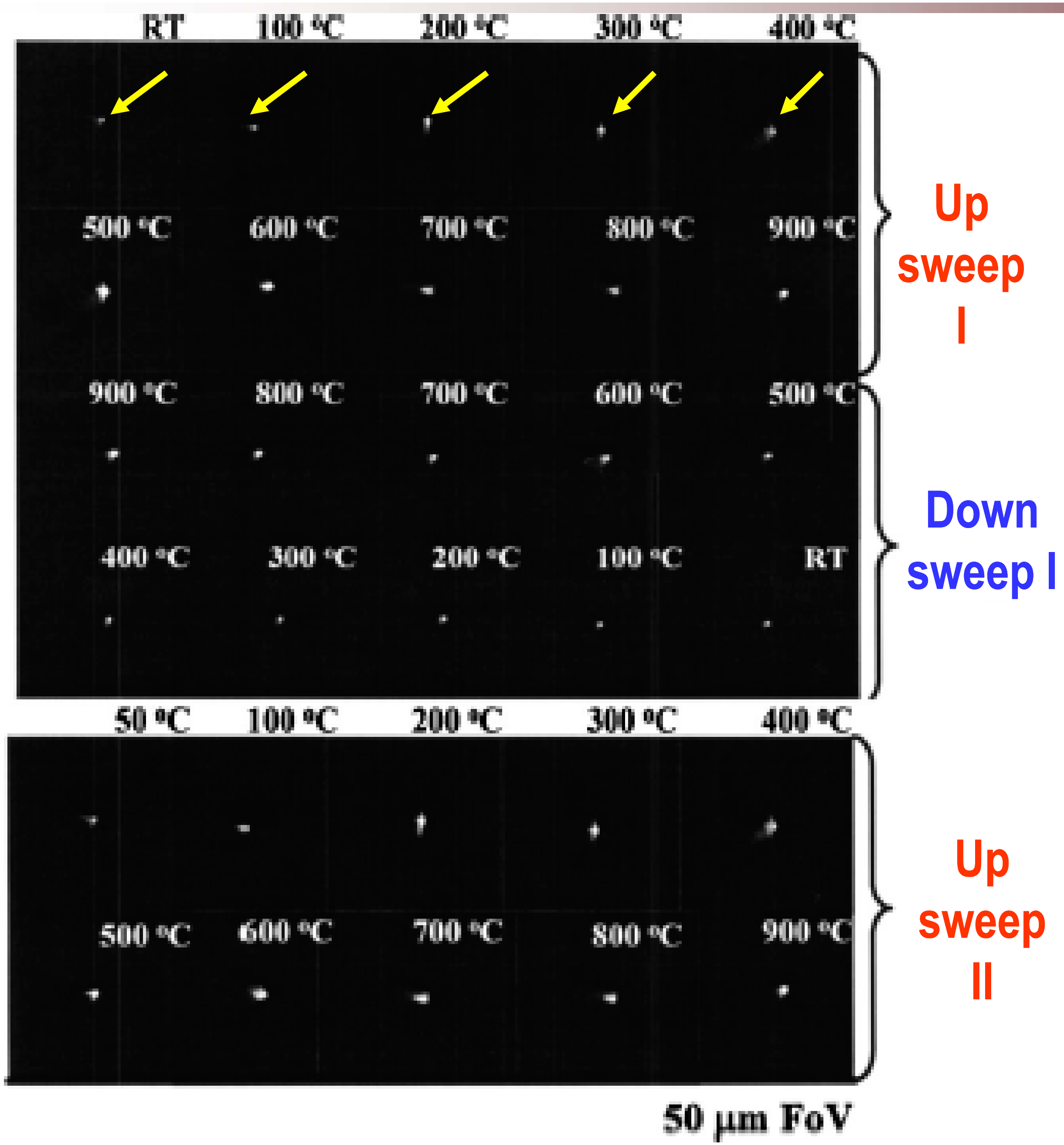


PEEM

CNT film on 2 nm Fe Catalyst Layer



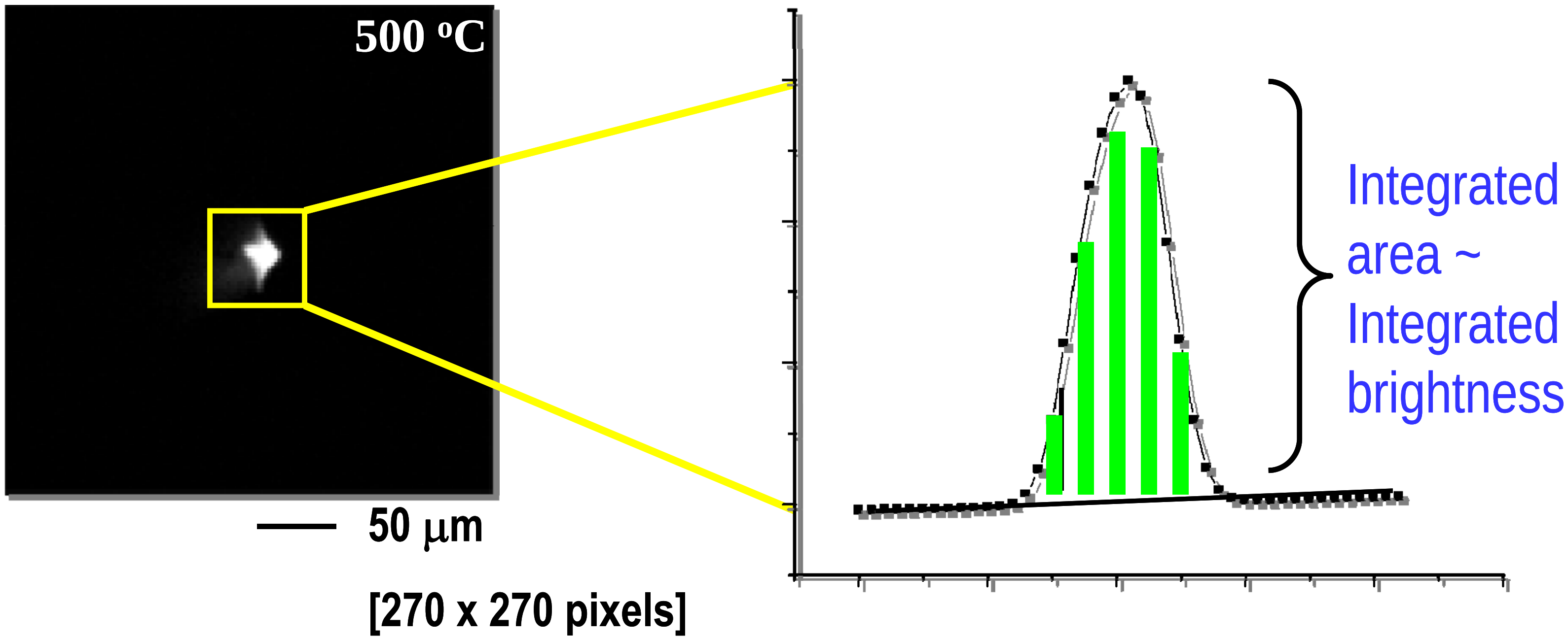
0.85 kV MCP, LLL Camera Gain, 1.4x10^{-8} Torr, approx. 150 μm FoV, 950° C



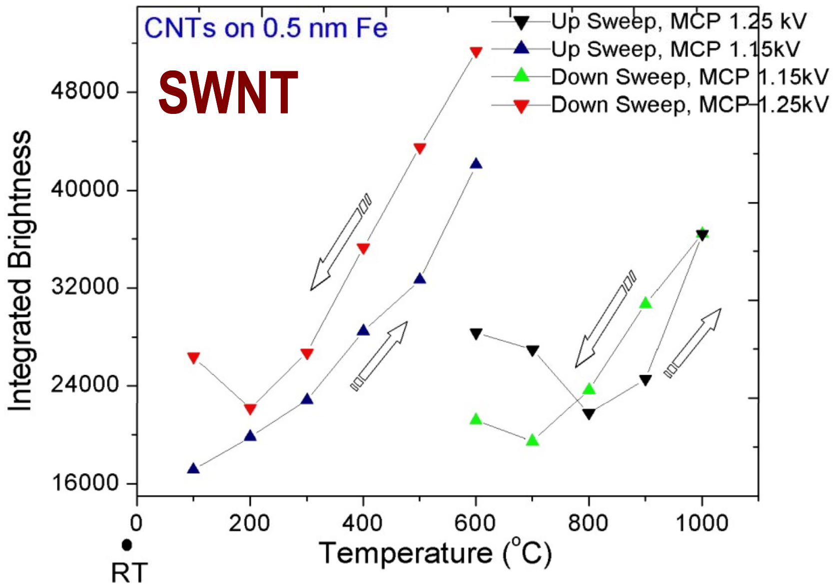
Role of adsorbates: thermal adsorption/ desorption

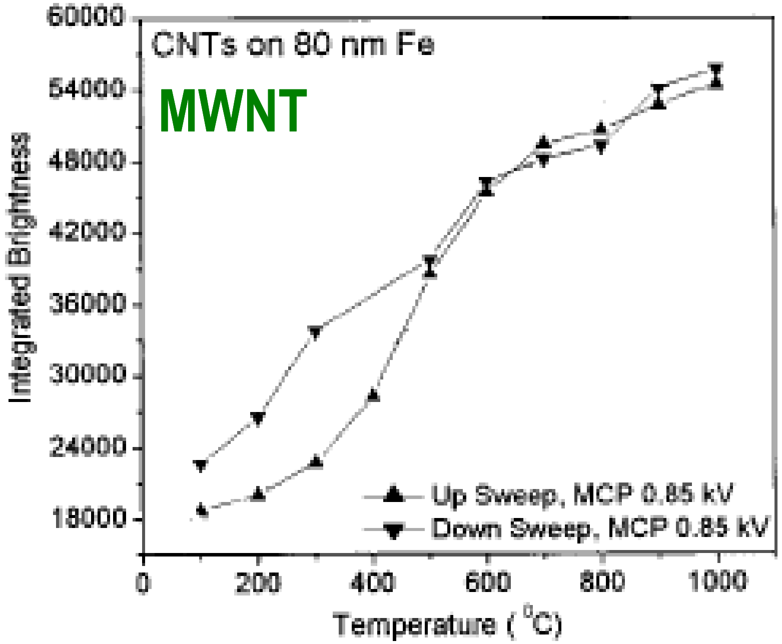
Predictable but weak temperature dependence *i.e.* the emission intensity increased from room temperature up to 900 ºC and decreased on down sweep with a little hysteresis. In addition, it demonstrates the role of adsorbates in field emission enhancement. This is because after thermal cleaning (or desorption) of the surface of the emitter, states due to adsorbate do not dominate as effectively.

Sampling → Histogram → Integration



Variation of Integrated Brightness: Temperature Sweep





Gupta, Wang *et. al.* APL **86** (2005); [VJNST].

Increasing Temperature…

- **increasing number of tunneling electrons**
- **some tunneling from thermally excited states**
- **very few are emitted from crossing the barrier**

$$j_{Tot} = j_{FE} + j_{TEx} + j_{TE}$$

$$j_{FE}(E) = \frac{C_1 E^2}{\Phi} \exp\left(\frac{-C_2 \Phi^{3/2}}{E}\right)$$

$$j_{TE}(T) = \frac{4\pi m_e e}{h^3} (kT)^2 \exp\left(-\frac{\Phi}{kT}\right)$$

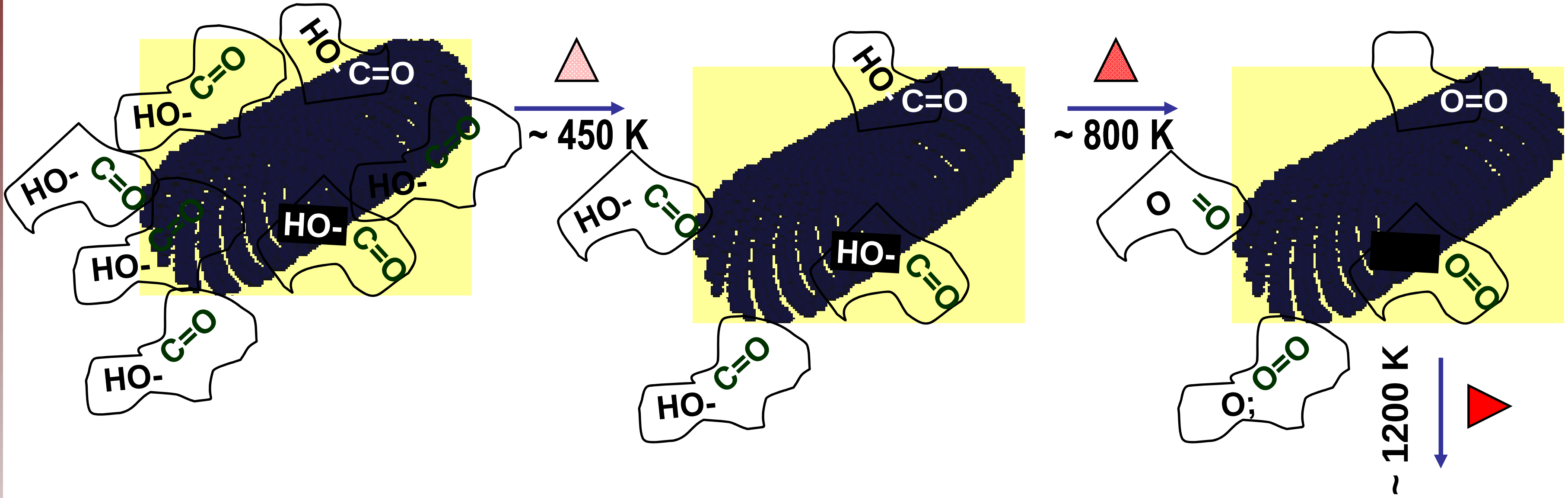
$$j_{TFE}(T, E, \varphi) = j(o, F, \varphi)\left(\frac{\pi k_B T / d}{Sin(\pi k_B T / d}\right);$$

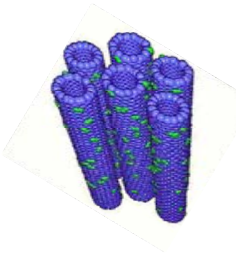
$$where \quad d = 9.3x10^{-9} E / \phi^{1/2}$$

For moderate fields, the temperature contribution is minimal: $j_{TFE} = j_{FE}$ (1.02-1.27) for 300-1200 K.

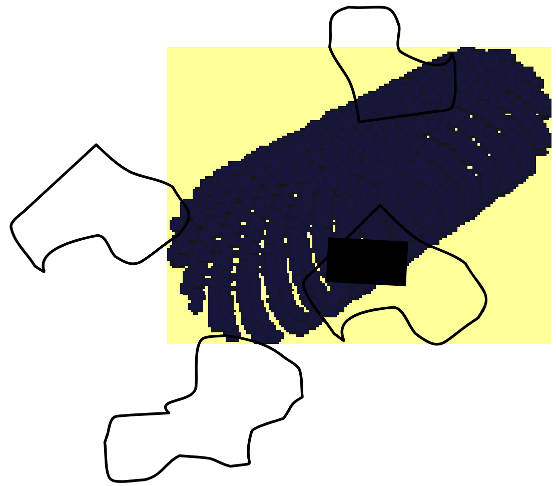
Note: assuming: [IB $\propto$ j]

contd… Thermally desorbed 'n' adsorbed species



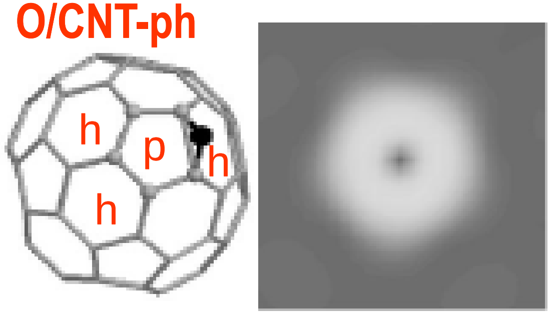


RECENT EXPERIMENTS HAVE SHOWN THAT SINGLE-WALLED CARBON NANOTUBES ARE SO SENSITIVE TO OXYGEN THAT THE ADSORPTION OF EVEN A FEW ATOMS (SHOWN IN GREEN; left) CAN CHANGE SEMICONDUCTING TUBES INTO CONDUCTORS.



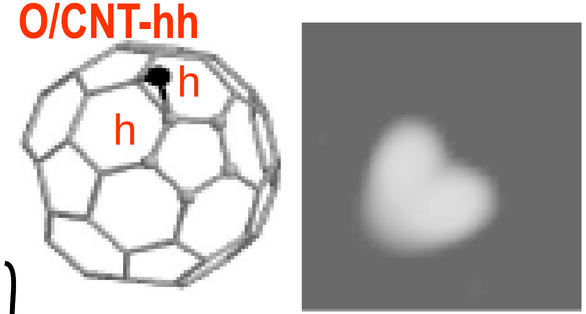
Interpretation in terms of ‘O_x’ adsorbate specie at the NT cap

a) **O/CNT-ph**

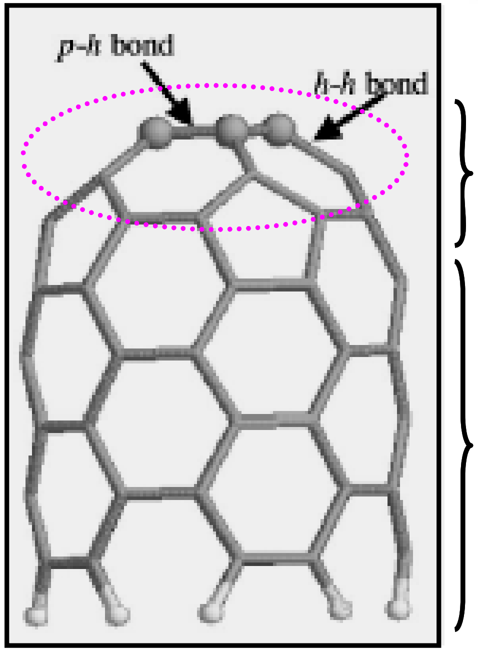


E_b (eV) = 6.73

b) **O/CNT-hh**



E_b (eV) = 6.60

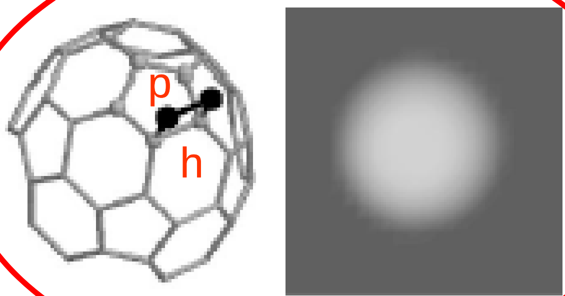


cap

body

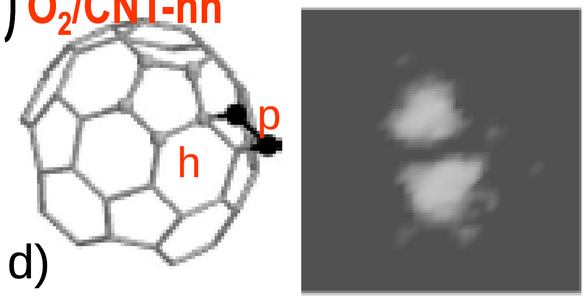
c) **O_2/CNT-ph**

E_b (eV) = 1.66



E_b (eV) = 3.02

O_2/CNT-hh



d)

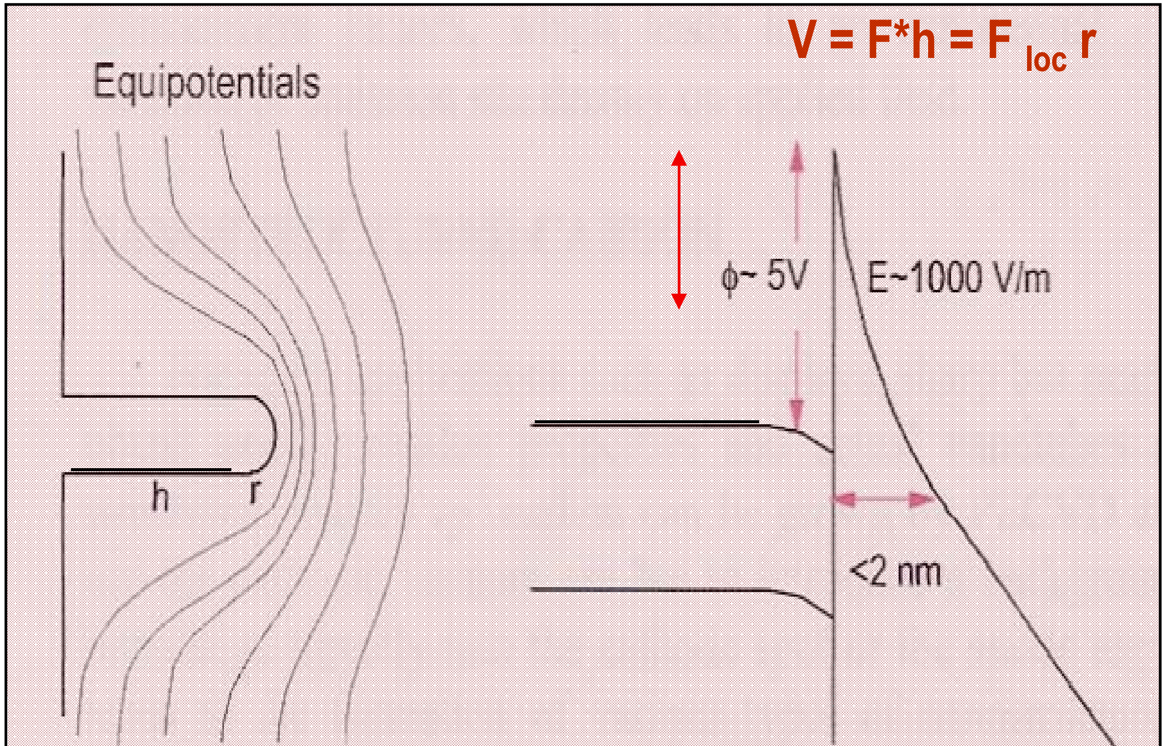
Carbon

Oxygen

E_b (eV) = - E (O_x / CNT) + E (CNT) + E (O_x); x = 1 or 2

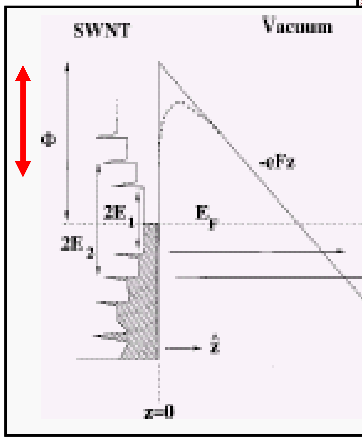
Park et. al. PRB 64, 125401 (2001).

Interplay of β, Real (local) work function, and barrier height

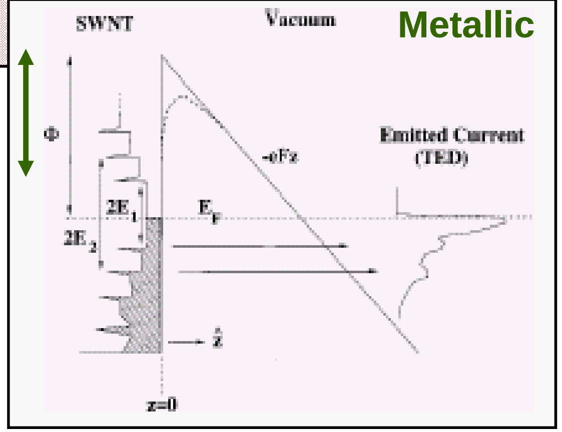


$V_{max} = -3.79\ F_{loc}^{1/2}$ eV

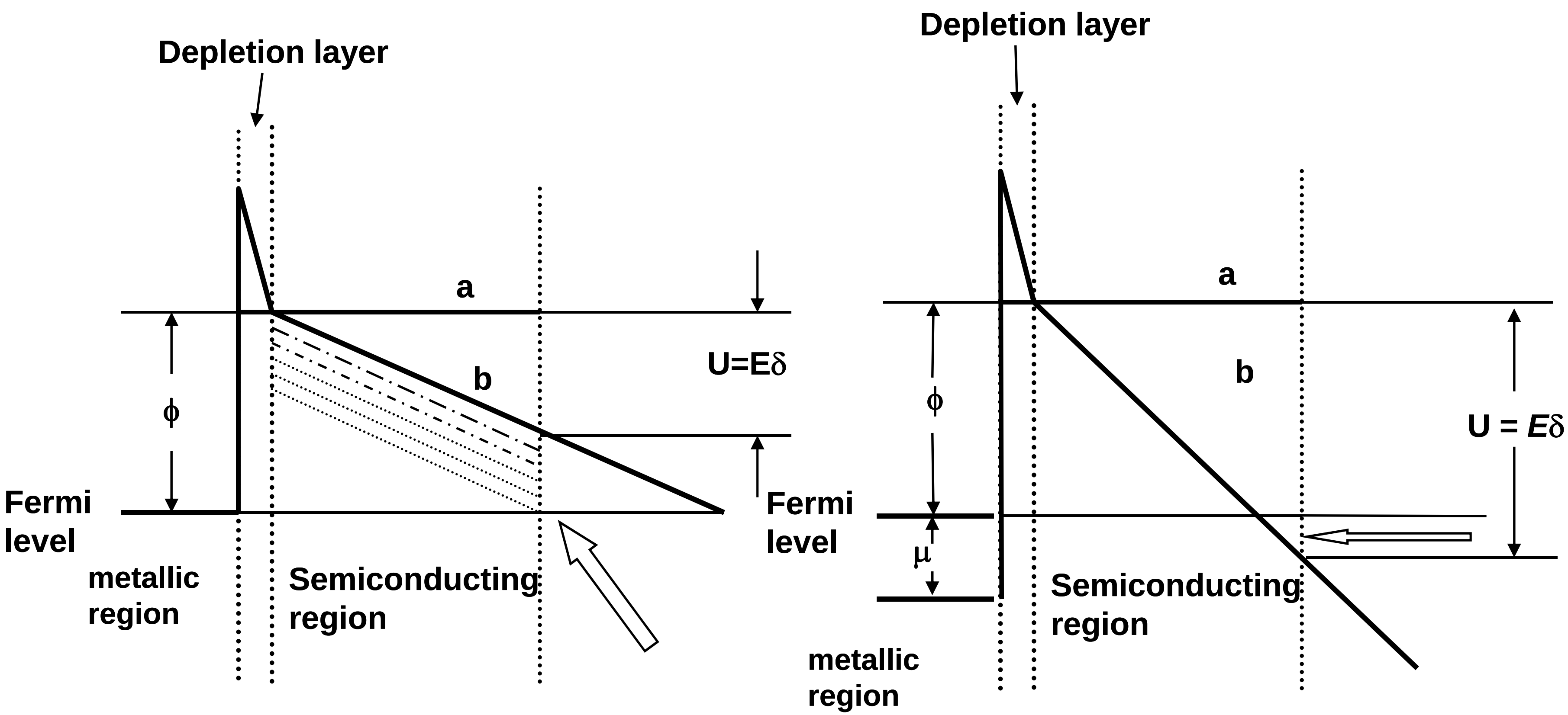
Semicond.



Metallic



Two-process Model: Electron Field Emission mechanism in Carbon Nanotubes

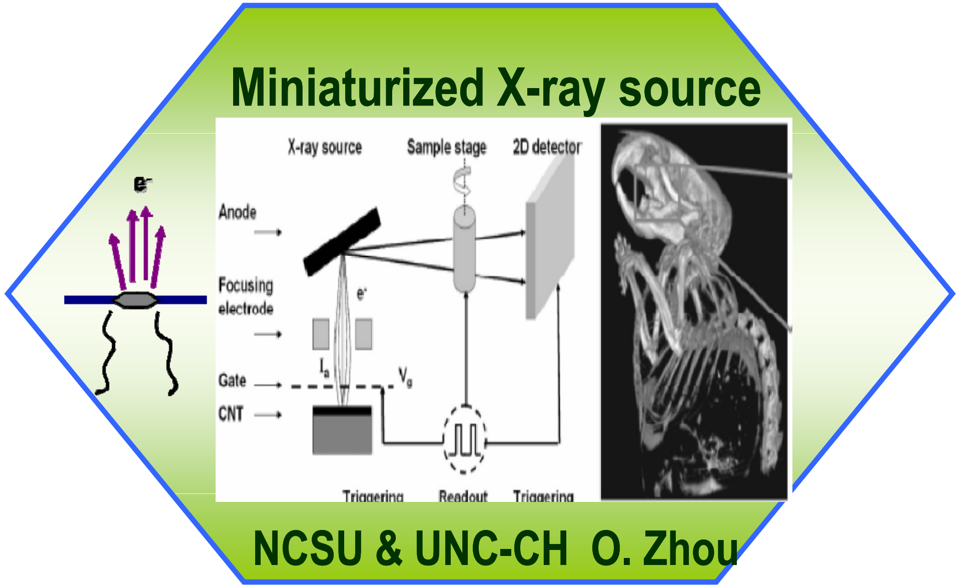


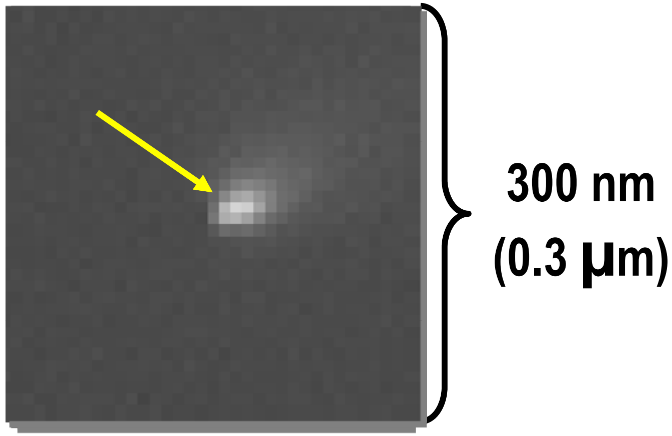
$$k(E) = \{\exp(-\frac{\vartheta - U}{\varepsilon_0}) \quad \vartheta - U > 0$$

$$\{ \quad 1 \qquad\qquad \vartheta - U \leq 0$$

Bright emission sites

These ultra bright electron emission sites which can be used in micro electro mechanical systems (MEMS) or (NEMS) for gas sensing application and as an intense miniaturized X-ray source.





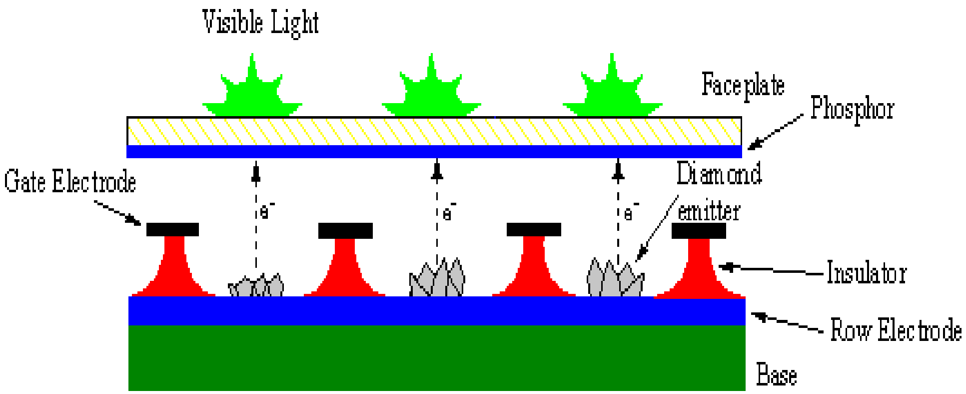
1.100 kV
dia. < 16 nm
J ~ 10^4 A/cm^2

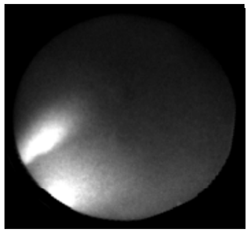
An emission microscope image of the electron emission from a single site on a nanocrystalline diamond surface.

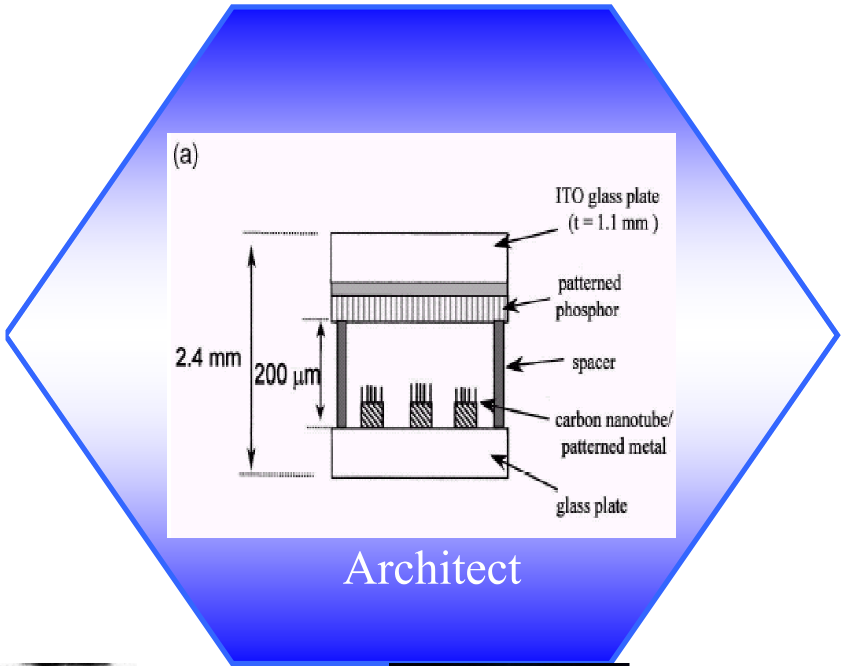
Comparison/Conclusion

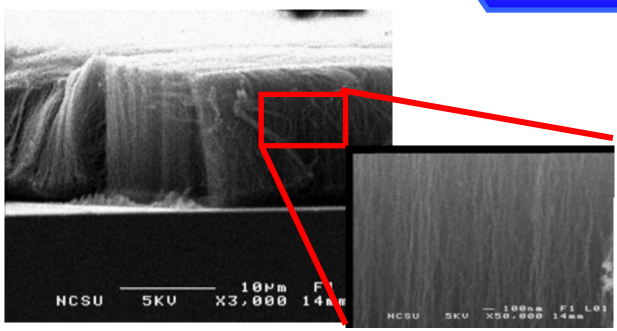
CNT-based √

Diamond-based ⊗



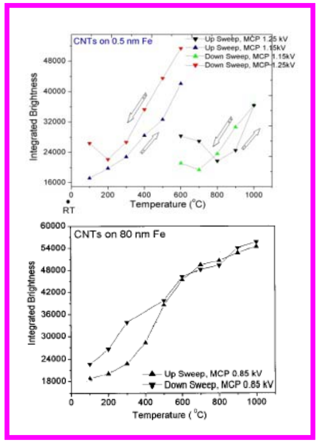






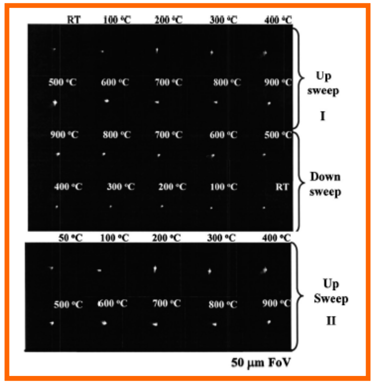
Summary: Part II

- *A contrasting comparison between SW and MW nanotubes is made*



- *Vacuum nanoelectronics*

Role of adsorbates in enhancing the field emission from carbon nanotubes is demonstrated: Temperature dependent electron emission imaging (T-FEEM)



- *Thermionic component to field emission, from nanotubes was also suggested, though weak (~ 15 %), which is proposed to use as a thermionic energy converter (TEC).*

$$j_{TFE}(T, E, \varphi) = j(o, F, \varphi)\left(\frac{\pi k_B T / d}{Sin(\pi k_B T / d}\right);$$

$$where \quad d = 9.3x10^{-9} E / \phi^{1/2}$$

For moderate fields, the temperature contribution is: $j_{TFE} = j_{FE}$ (1.02-1.27) for 300-1200 K.

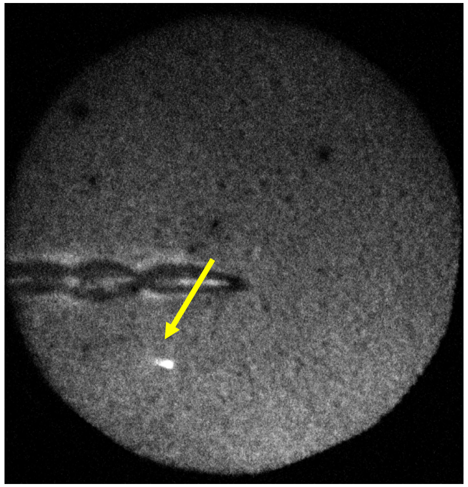
However, my crystal ball is not good enough to see which application(s) will really make it!

?

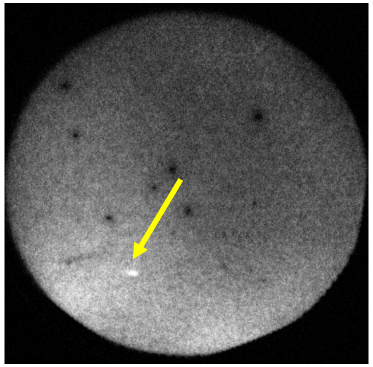
Stay tuned…

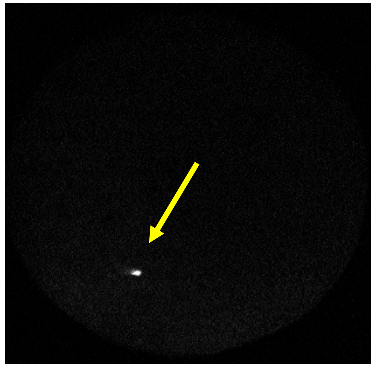
Field electron emission microscopy (T-FEEM): CNTs

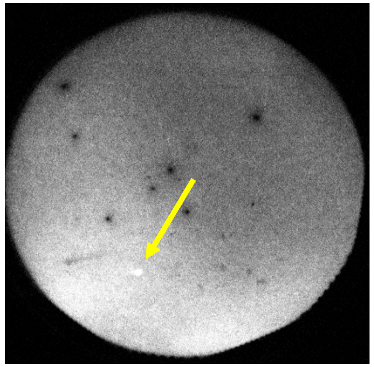
PEEM



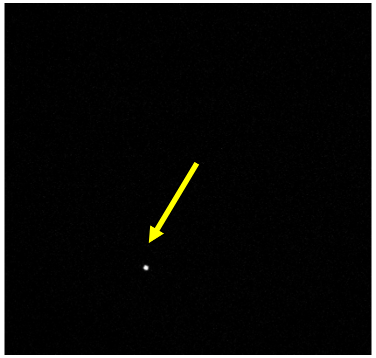
Field emission measurements at various temperatures

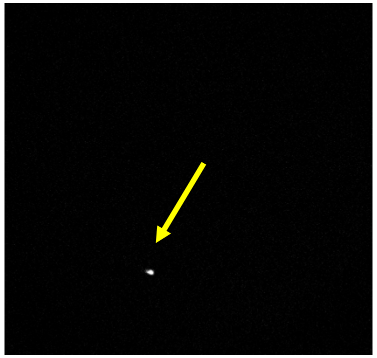


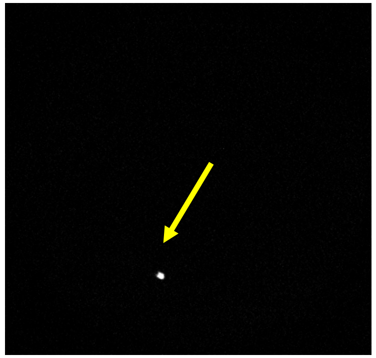




25 ° C **90 ° C**







150 ° C **200 ° C** **300 ° C**

[Pressure changes from 6.6 x 10^{-9} to 8.1 x 10^{-7}as temperature increases

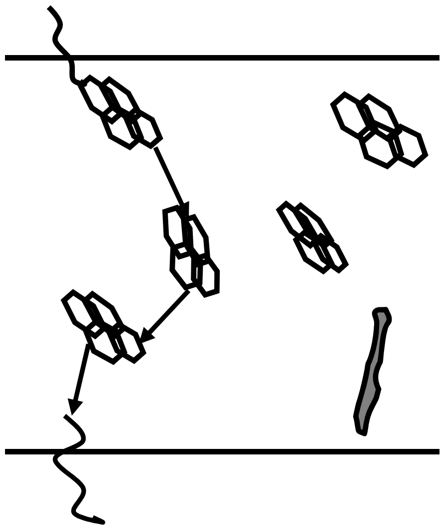
FoV: 20 μm and channel plate voltage of 1.55 kV]

- Not many emission sites
- Role of adsorption on field emission
- Intensity fluctuations - flicker

Gupta *et. al.* DRM submitted 2004

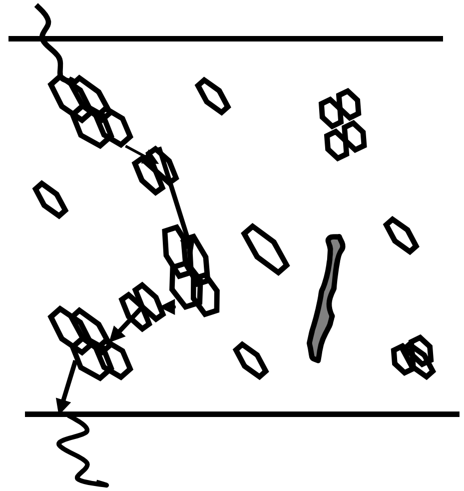
Microstructural Variation as a function of Nanostructuring

Un-doped



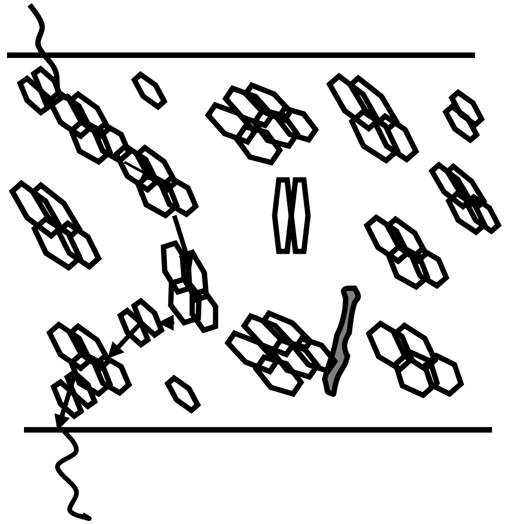
Large hopping distance - low spatial or interconnectivity

Irradiated



Introduction of clustering - reducing hopping distance

Doped



Re-ordering due to increase in cluster size - further reduction in hopping distance