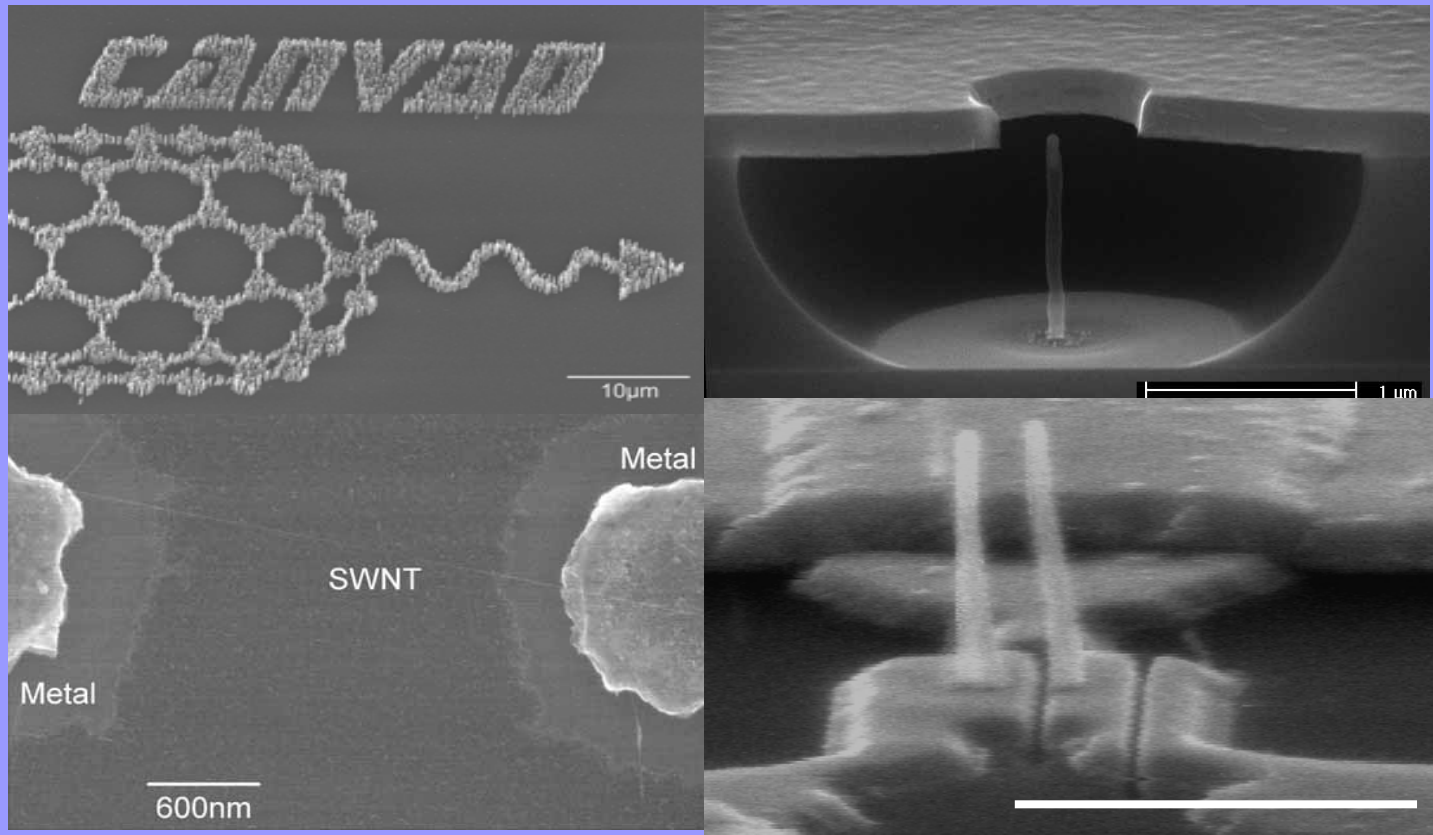


Carbon Nanotubes for Electronic Applications?



WI Milne
Engineering Dept,
Cambridge University

People involved at CUED plus outside Collaborators

- **CUED**

Ken Teo

Gehan Amaratunga

John Robertson

David Hasko

Mark Mann

Martin Bell

Nalin Rupesinghe

AunShih The

Ming-Hsun Yang

Sara Vieira

Ian Bu

X.Wang

Thales R & T
Advance Nanotech
T.I.T

Hitachi

T.U.Denmark

Samsung

CEA, Saclay

University of Lyon

University of Fribourg

Univ of York

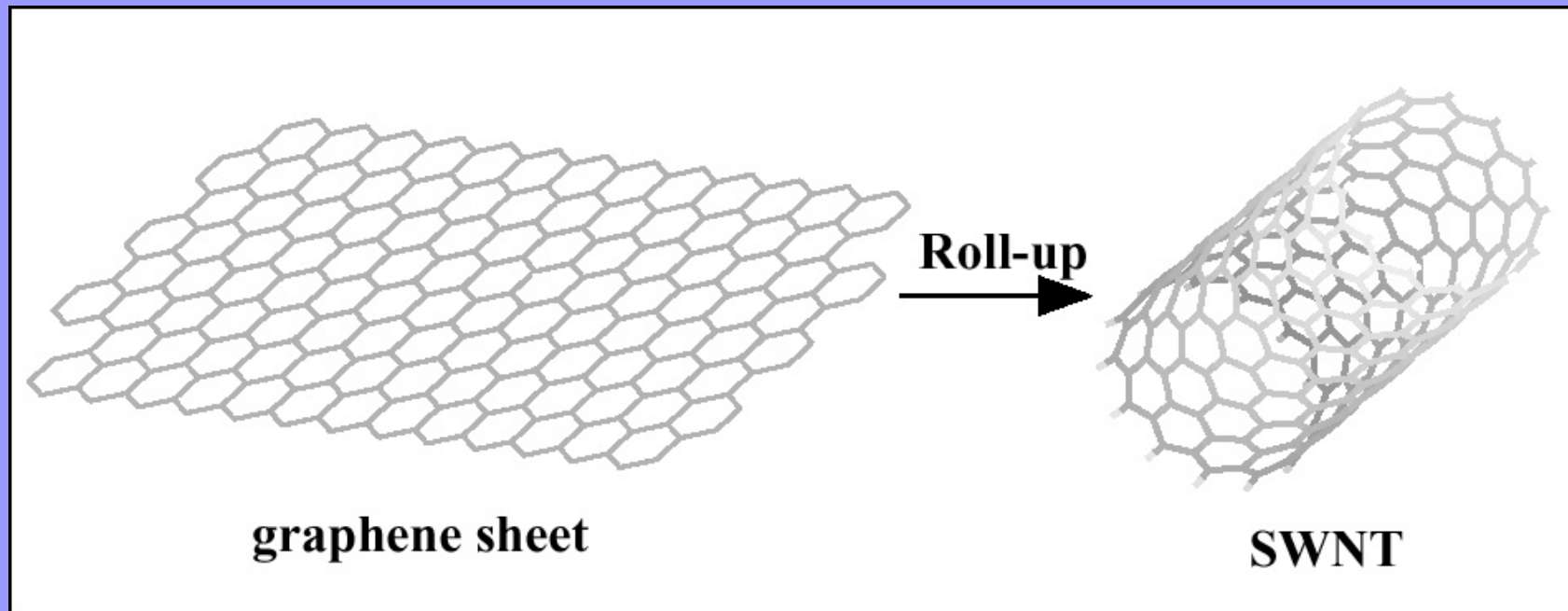
Various EC consortia inc

PROMENADE, CANVAD,
NANOLITH, DESYGN-IT,
CARDECOM, CANAPE,
NANORAC, CANDICE etc

- Introduction
- Growth of Carbon Nanotubes
- Optimisation of CNTs
- Near Term Applications
- Longer Term
- Conclusions

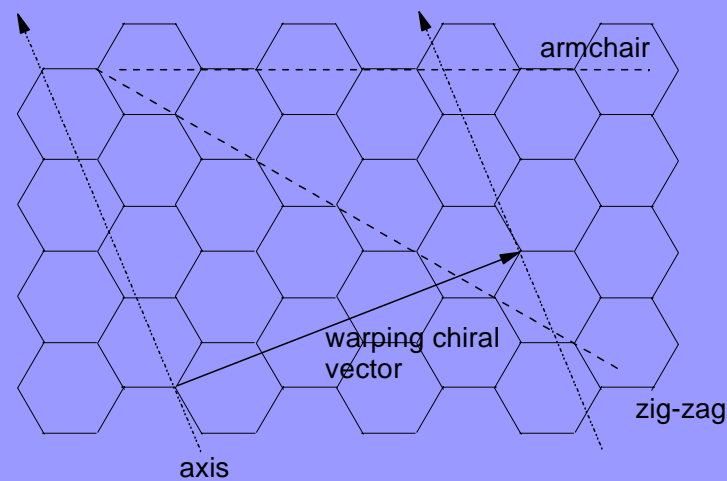
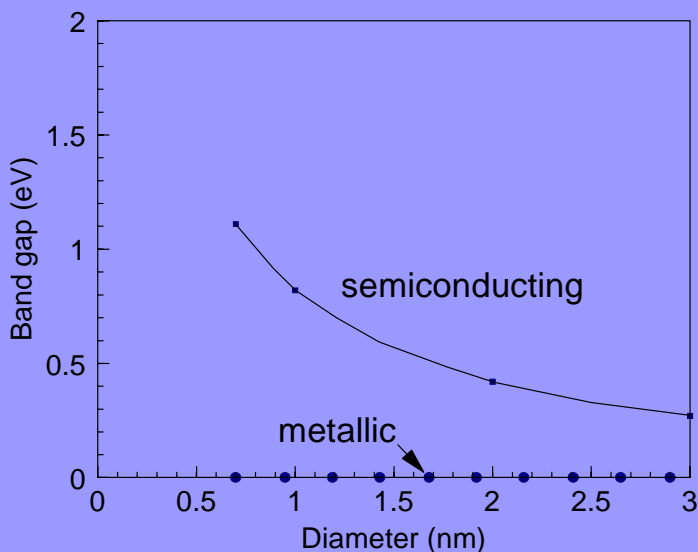
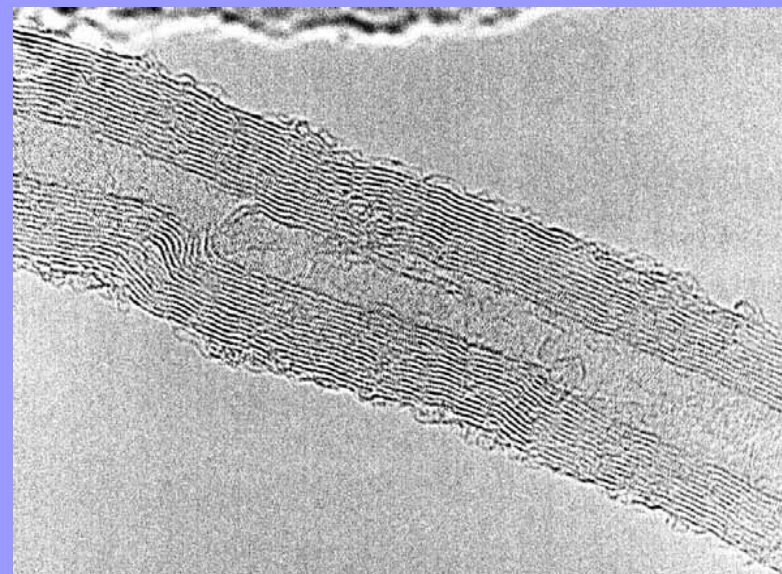
What are CARBON Nanotubes

- Single wall nanotubes can be semiconducting!



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

- Rolled up graphite sheets
- no unsatisfied surface bonds
- Single walled or multi-walled
- Metallic or semiconducting
- Band gap of SWNTs = $f(\text{chirality, diameter})$ or 'wrapping vector' (n,m)
- Multi-walled are metallic



Uniqueness of CNTs

Unique properties of

- Sharp - aspect ratio – **field emission, electrical composites**
- Highest current density 10^9 A/cm² – **Vias, FE,**
- Ballistic electron transport - **FETs**
- Highest Young's modulus, ~1TPa - **composites**
- Highest thermal conductivity, 4000 W/m.K - **composites**
- Electrode potential range/surface area – **sensors, supercaps**

Growth of Carbon Nanotubes

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

Synthesis Techniques

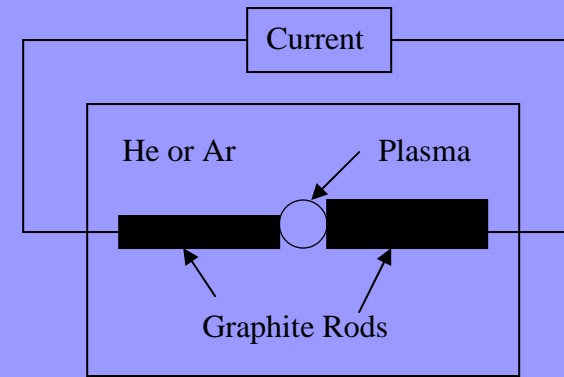
1. Arc-discharge Method

- Producing MWNT & SWNT
- Two graphite rods are used as electrodes and He or Ar gas used for inert atmosphere condition during arc-discharge

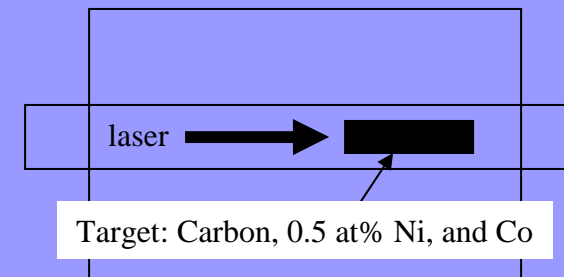
2. Laser Ablation Method

- Producing SWNT
- Intense laser pulses are utilized to ablate a carbon target containing 0.5at % of nickel and cobalt.

- * **Advantage** -Production of high quality carbon nanotubes
- * **Disadvantages** -High temperature process
-Grow carbon nanotubes in highly tangled forms with unwanted carbon and metal impurities.- need to purify
-Hard to control



(a) arc-discharge



(b) laser ablation



NONE

SEI

2.0kV

X16,000

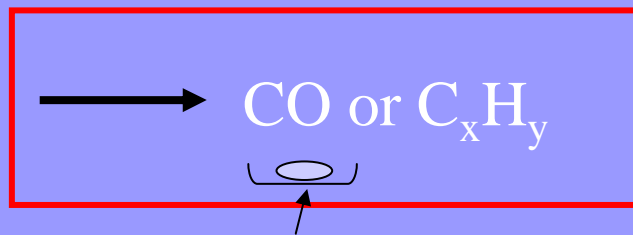
1μm

WD 6.5mm

Catalytic Chemical Vapour Deposition

Thermal CVD

550-900°C



Fe/Ni/Co catalyst on support or substrate

Plasma CVD

Anode



Cathode

At 500-900°C

Fe/Ni/Co on substrate

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

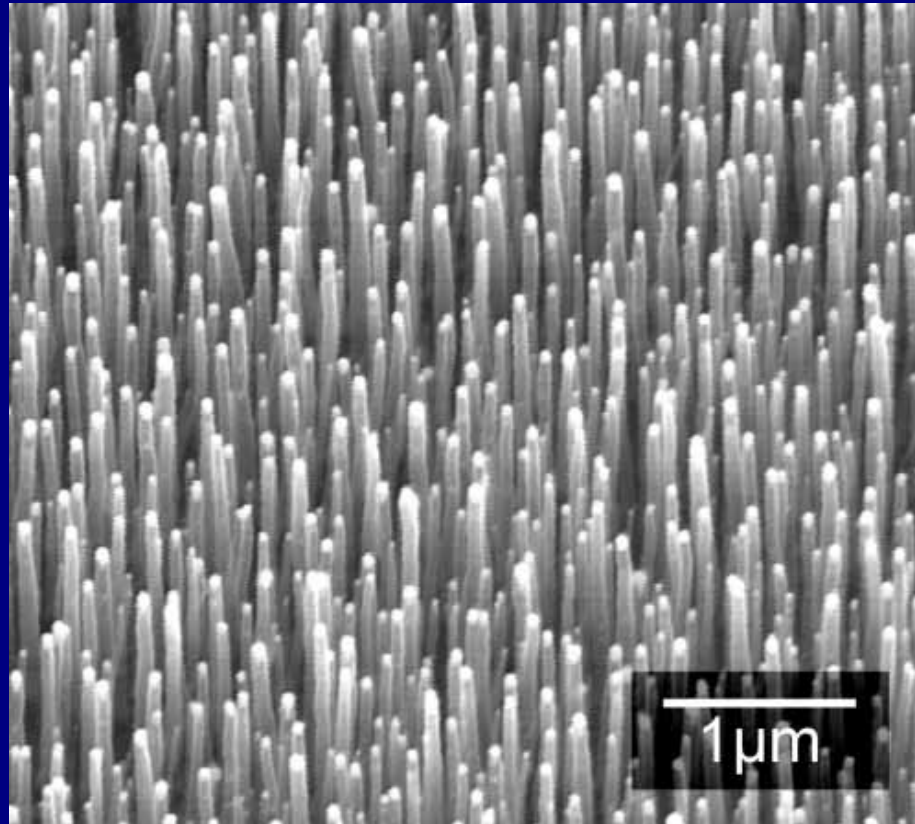
Disadvantages: expensive compared with arc

Growth Process of CNTs

CNTs grown from Ni clusters

Ni cataly

substrate



CN's

substrate

CNTs,

- **Step 1:** At agglomera
- **Step 2:** PE NH_3 is the

Bright dot at CNT top = catalyst cluster

CNTs by Plasma Enhanced CVD

- Aligned growth
- High yield
- Uniform
- Diameter/length control
- Selective growth
- Can be large area

PECVD references

HF+DC: Ren, Science **282**, 1105 (1998)

DC: Merkulov, APL **76**, 3555 (2000)

Microwave: Bower, APL **77**, 830 (2000)

DC: Chhowalla, JAP **90**, 5308 (2001)

ICP: Delzeit, JAP **91**, 6027 (2002)

Anode

Thermo
couple

Plasma

substrate

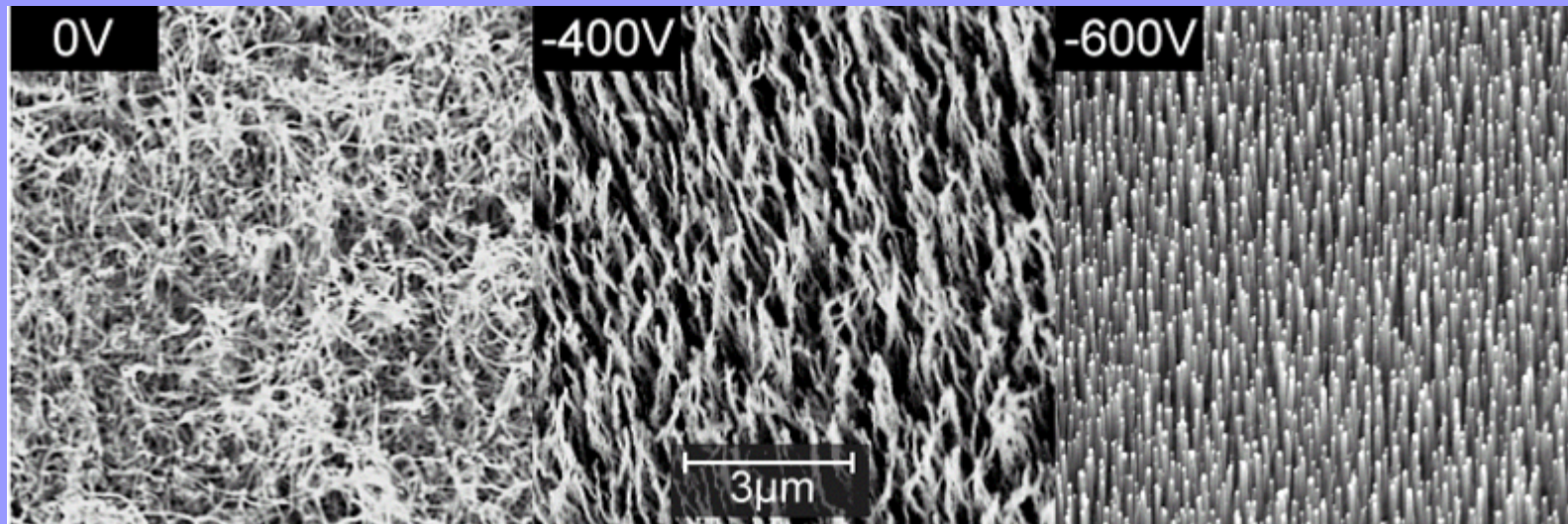
Heated
cathode

Deposition equipment
Is available from
Cambridsge Nanoinstruments



We use a PECVD Method of Growth for Multiwall CNTs-

*Influence of Plasma Voltage on the
Alignment of Nanotubes*



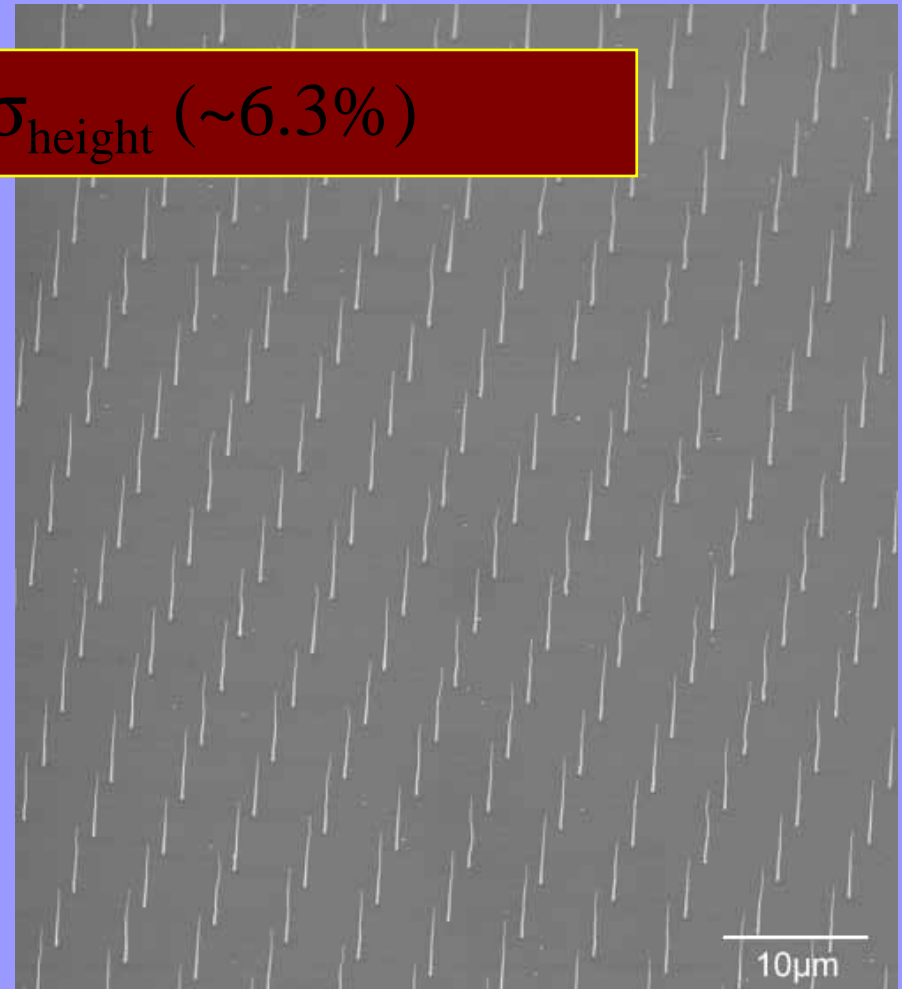
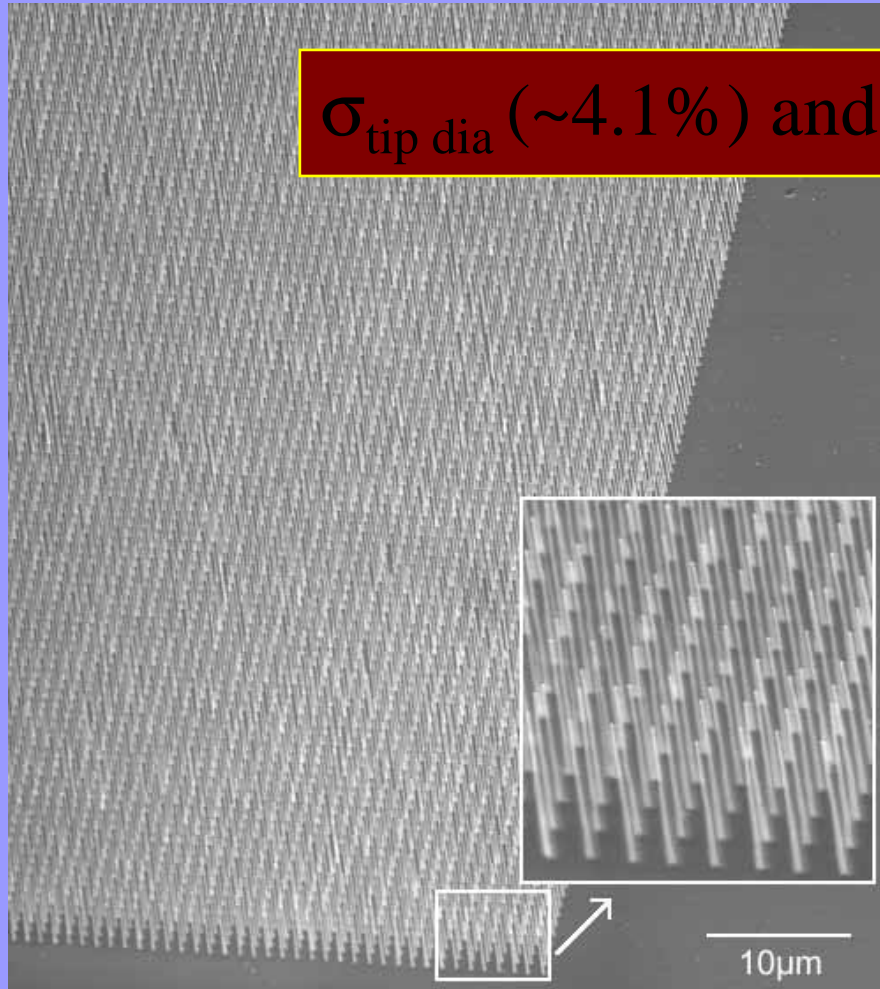
$$E = 0 \text{ V}/\mu\text{m}$$

$$E = 0.1 \text{ V}/\mu\text{m}$$

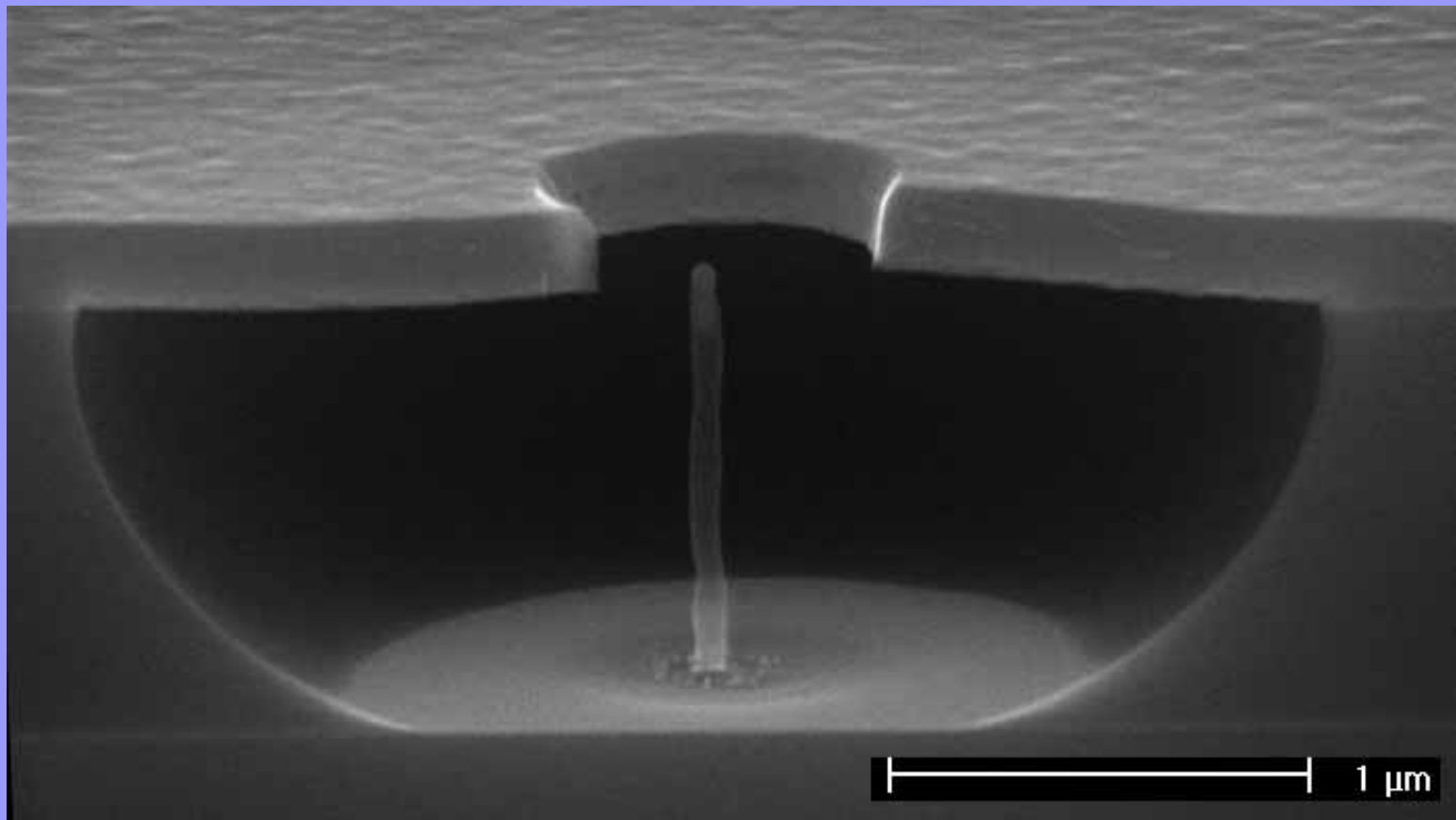
$$E = 0.35 \text{ V}/\mu\text{m}$$

Designable CNT Arrays

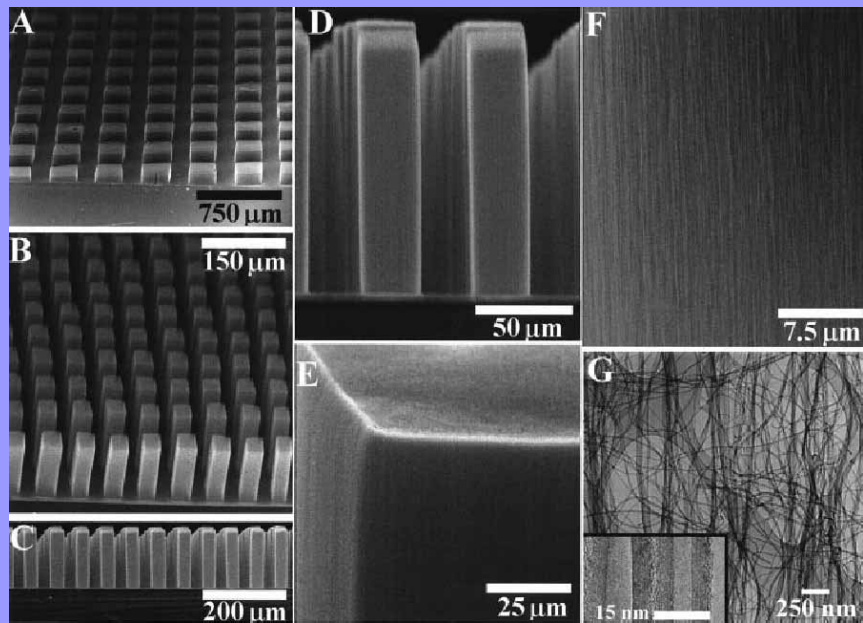
$\sigma_{\text{tip dia}}$ (~4.1%) and σ_{height} (~6.3%)



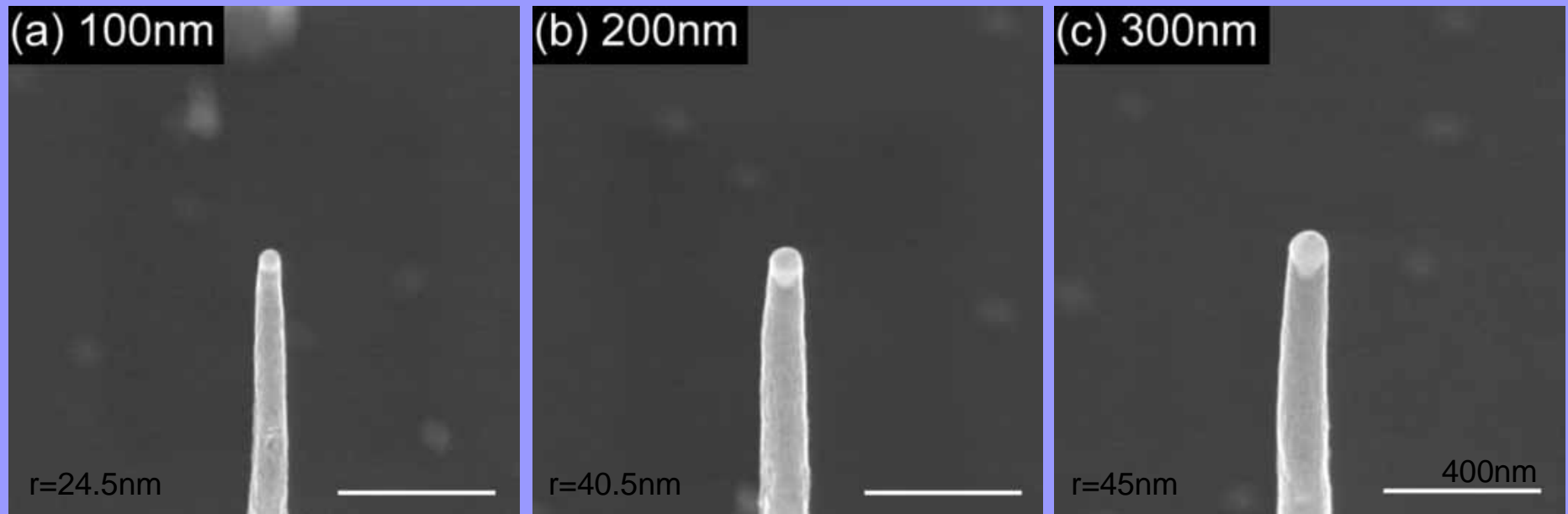
160nm litho, 10µm pitch, 5µm tall CNTs (45mins growth)



Fan et al, Science **283**, 512 (1999)



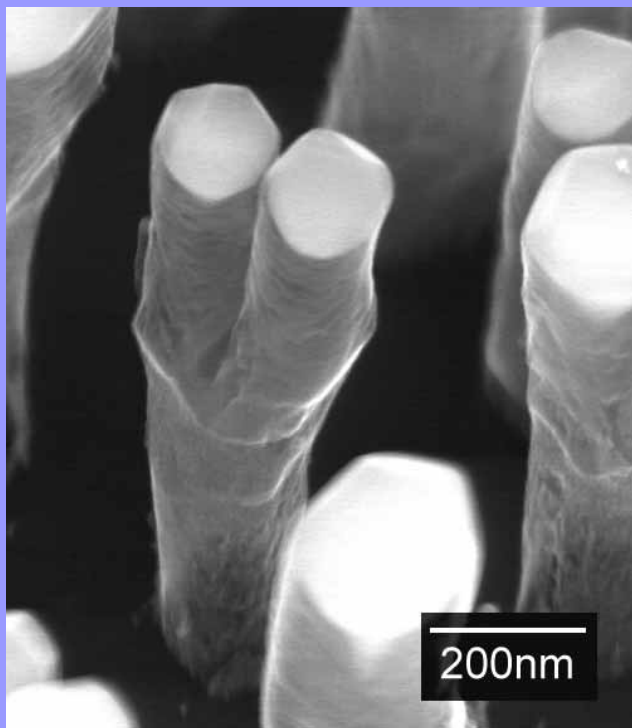
Regular tip shape



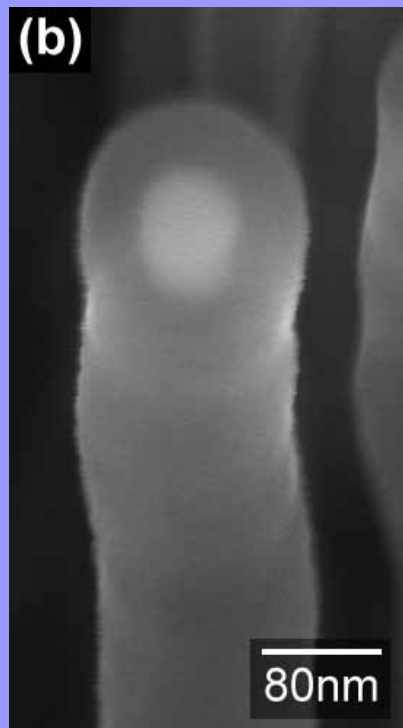
Different diameter CNT from different catalyst dot sizes

Hemispherical cap gives the whisker shape which agrees with $\beta = h/r$ theory

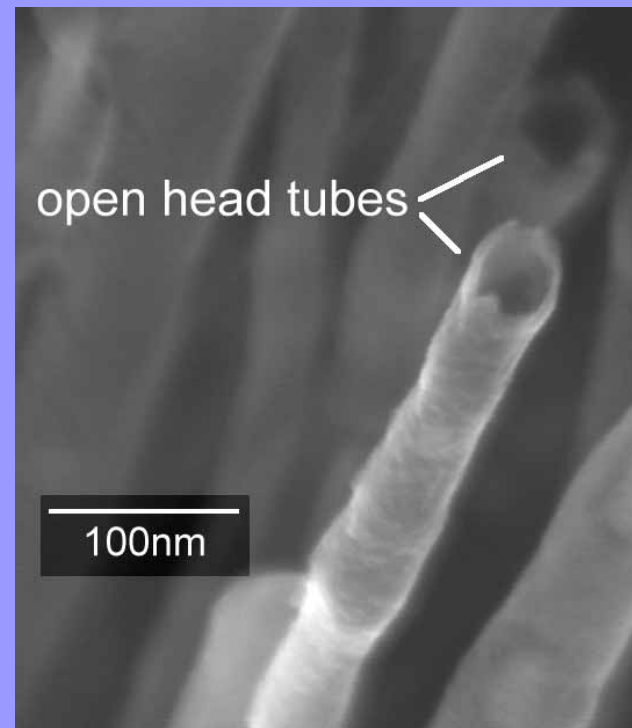
Other interesting PECVD structures



Branched



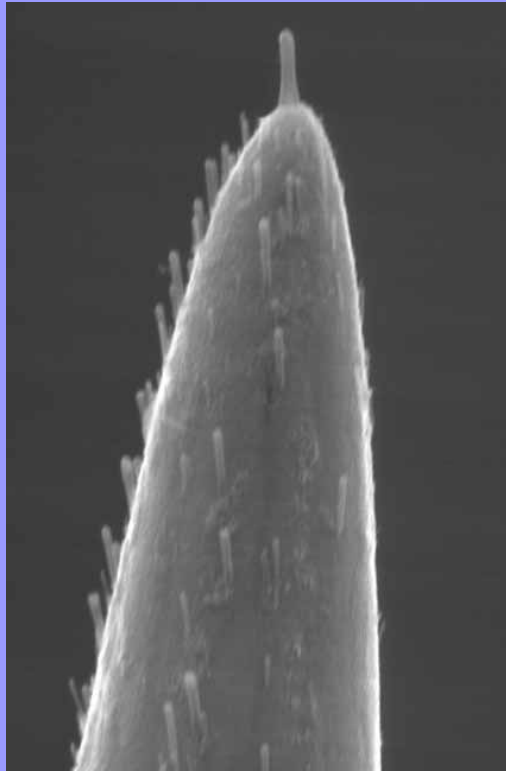
Coated



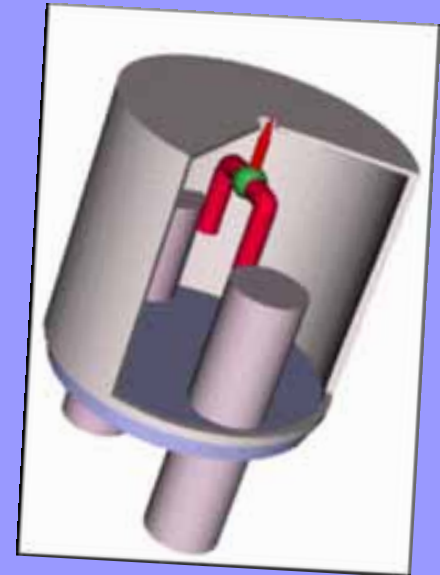
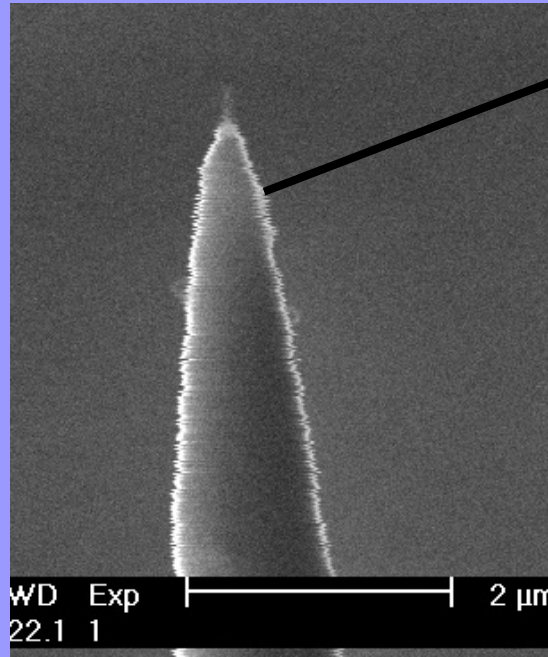
Open

Near term applications

- Field emission

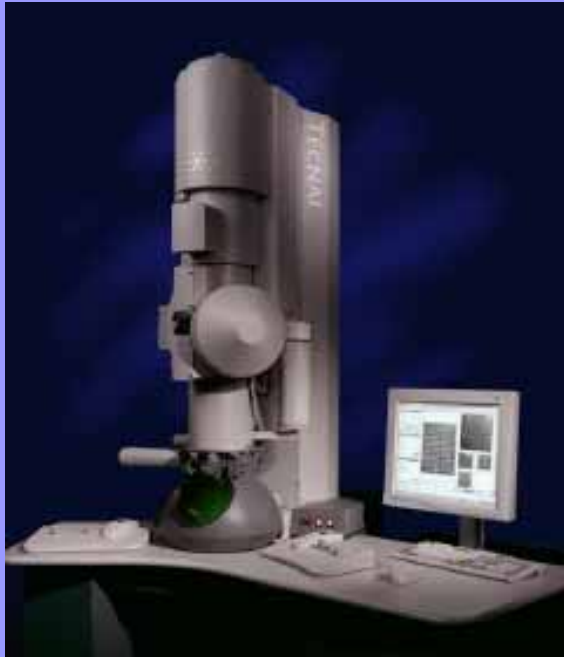


In collaboration with
FEI and York Univ.



Electron Microscopes

e- Guns for SEM

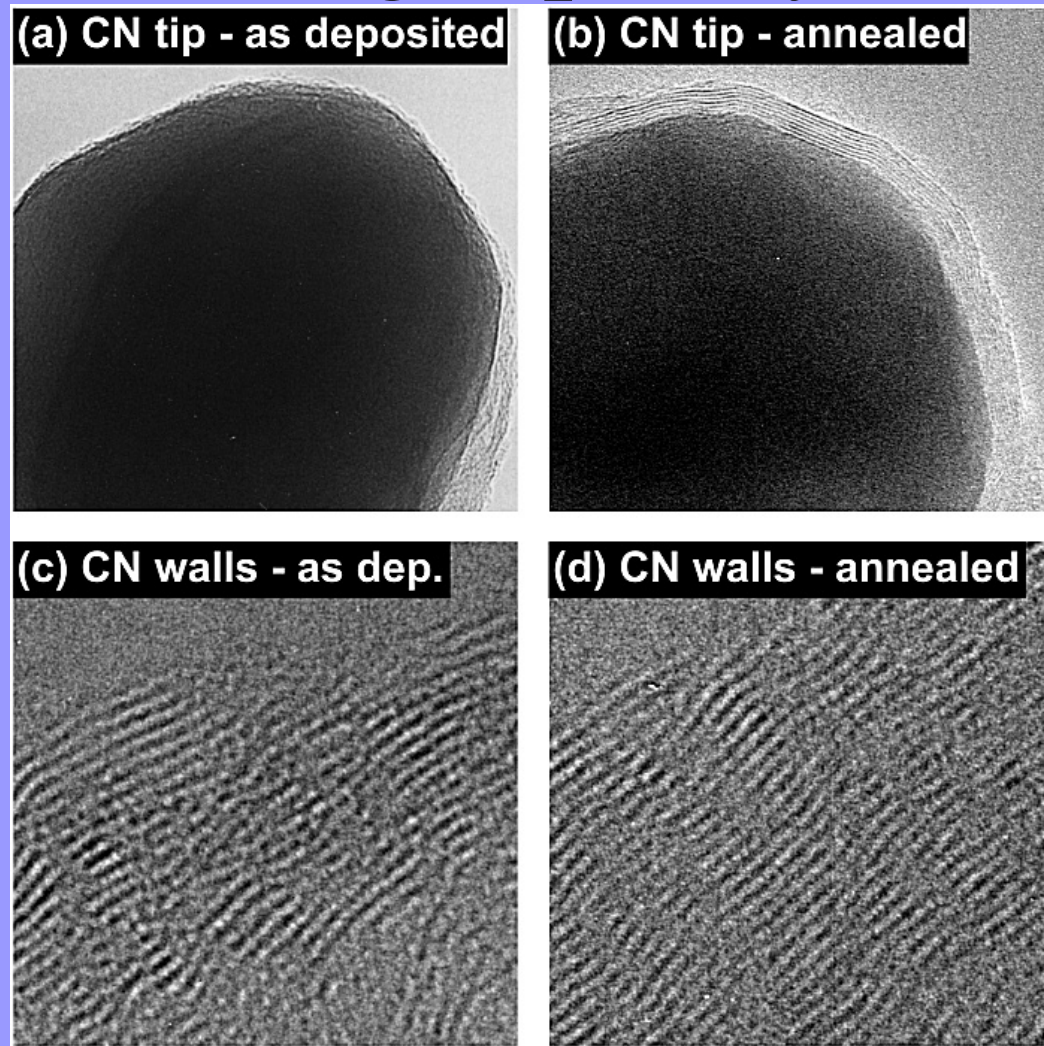


- Replace Si 'Schottky' emitters
- Use MWNTs due to greater stiffness
- High max current density
- Small source size – 2nm
- Narrow Energy Width – 0.25 eV
- High brightness = $3 \cdot 10^9 \text{ A}/(\text{m}^2\text{Sr.V})$
- N deJonge et al (FEI/Philips), Nature 420 393 (2002); JAP 95, 673 (2004)

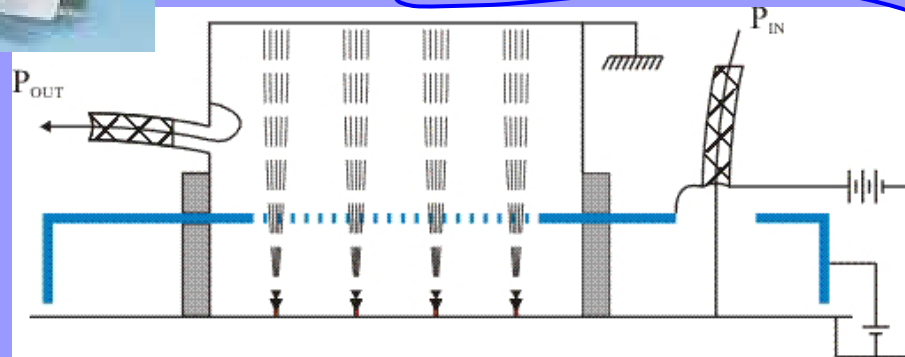
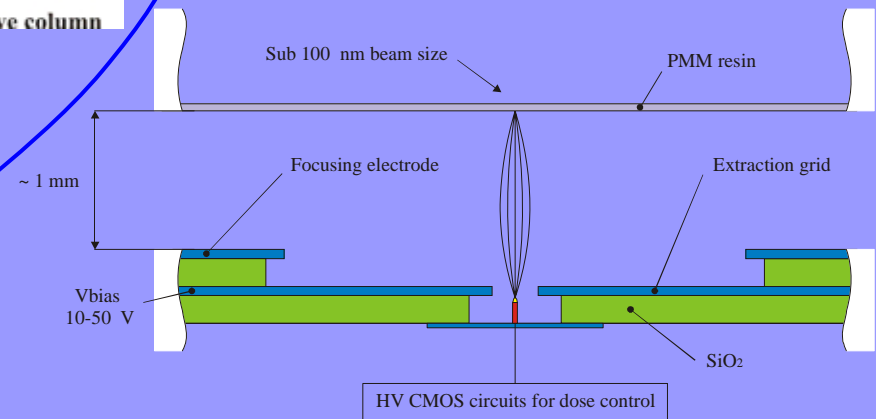
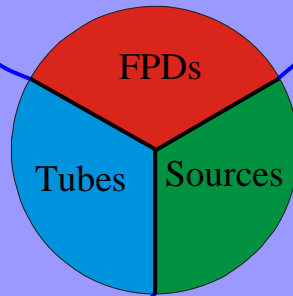
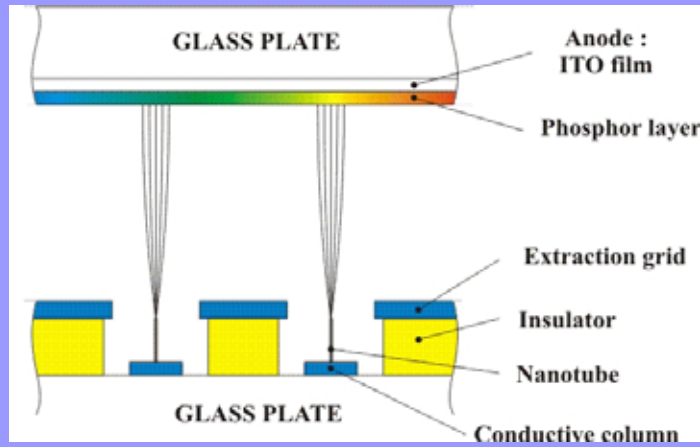
- Manufacturability
- Current stability

	Cold FE	Schottky	CNT
ΔE (eV)	0.25	0.7	0.25
r (nm)			2
B (A/Sr/m ² /V)	10^7	10^8	3×10^9

Towards high quality emitters

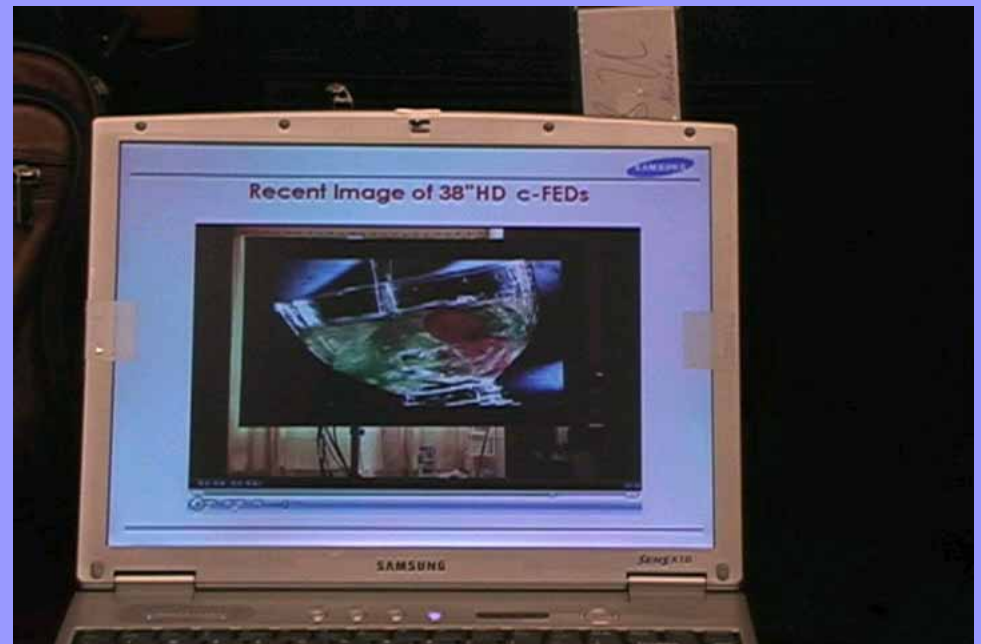


Other Field Emission Applications



SAMSUNG 38" Multi Colour CNT based FED

- Shows significant improvement since first shown in 2002
 - Dr.J. M. Kim SAIT(IVMC 2003)
- No line defects and Very few point defects



Longer Term Applications

Vias/Interconnects

Transparent Conductors

MEMS/NEMS

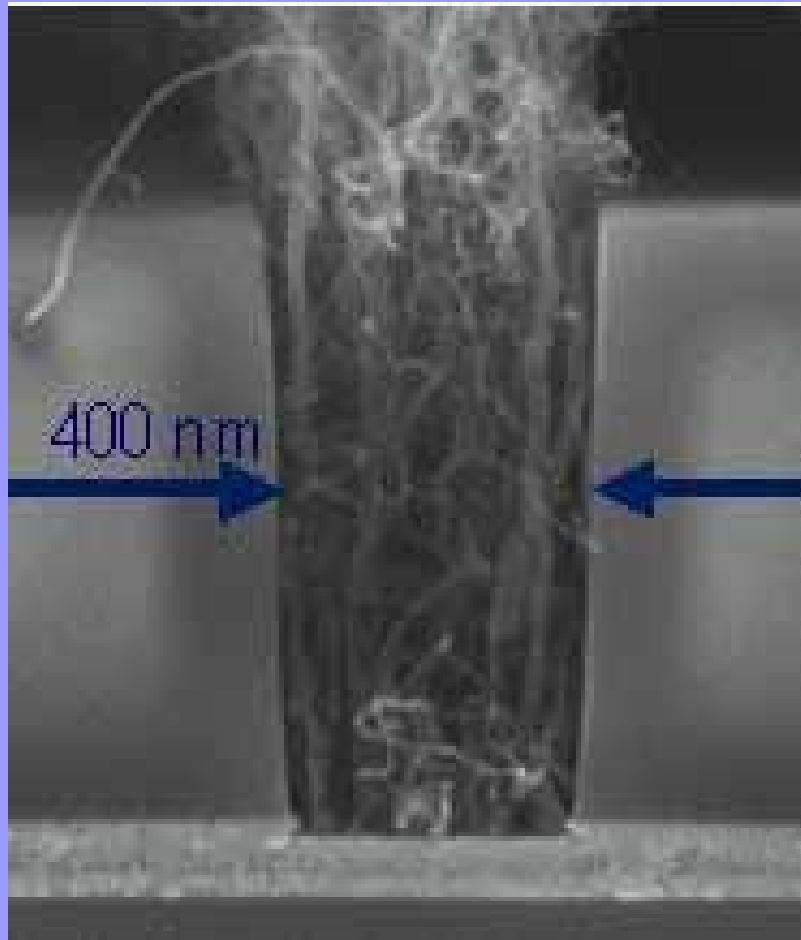
Bio/Gas/ Chemical Sensors

Transistors/logic

Solar Cells

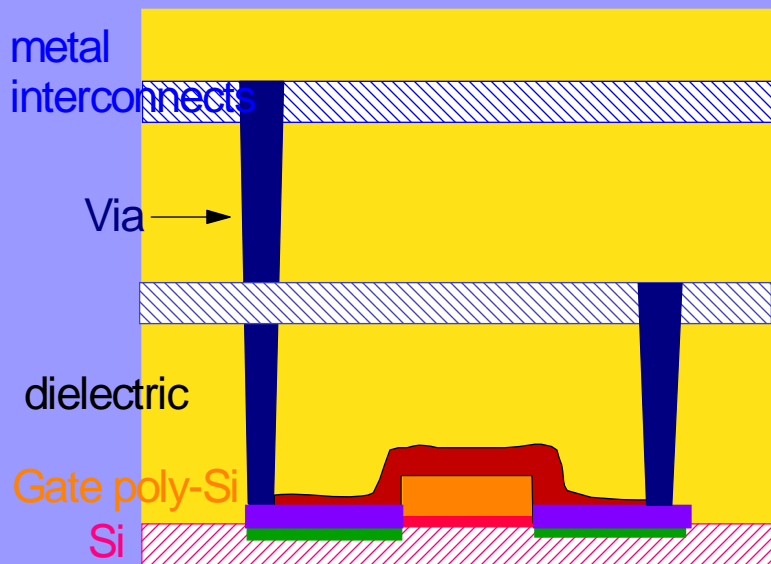
Energy Storage Devices

etc



Multiwalled nanotubes grown by catalyst mediated selective CVD in a via
from INFINEON WEBPAGE

Electronics – Interconnects in ICs



Cross-section of an Integrated Circuit

- Electromigration limits max current density in IC interconnects
- $J = 10^5 \text{ A/cm}^2$ (Al), 10^6 A/cm^2 (Cu)
- CNTs have strong covalent bonds – less electromigration

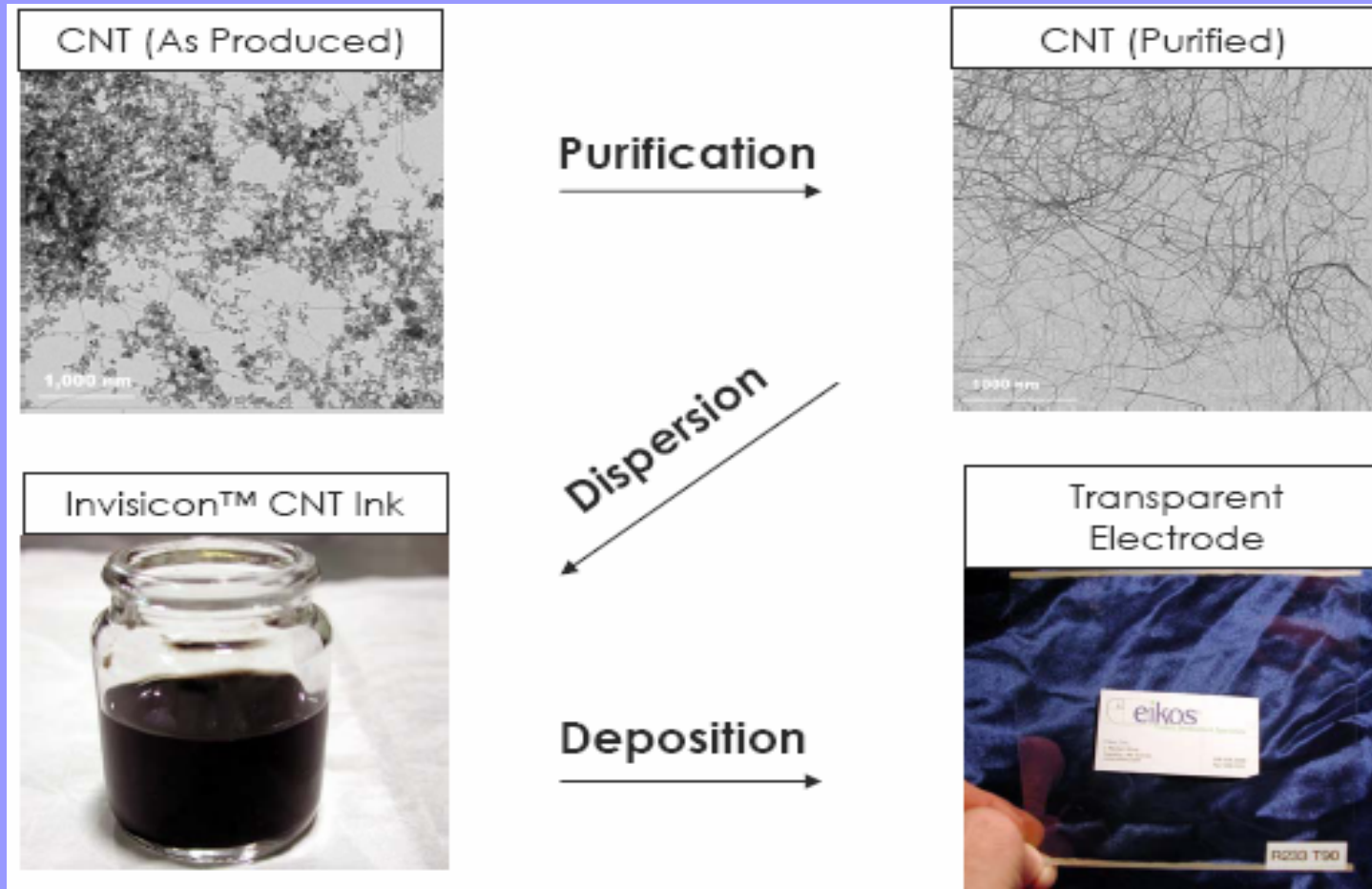
$$J_{\text{max}} = 10^9 \text{ A/cm}^2$$

- Vias - vertical growth ideal for PECVD
e.g. (Infineon) A P Graham, IWEP 2003
- Uses metallic MWNTs

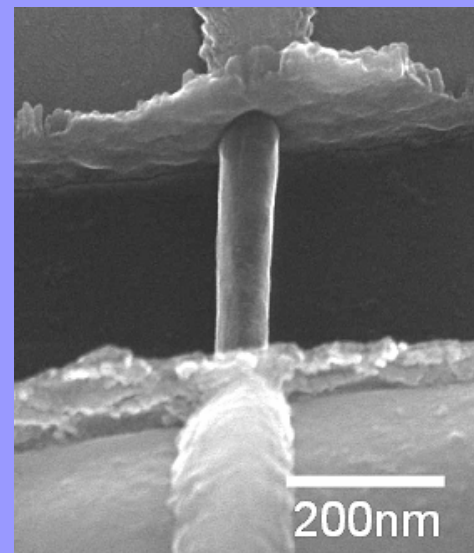
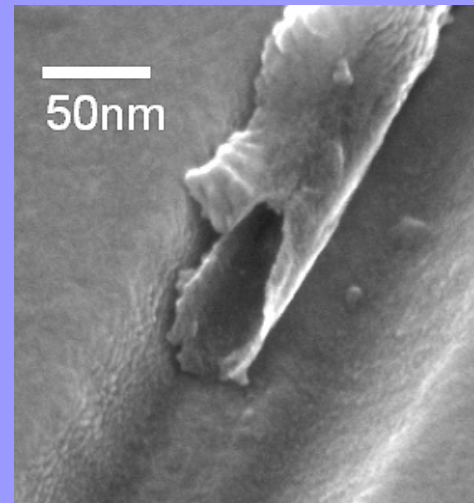
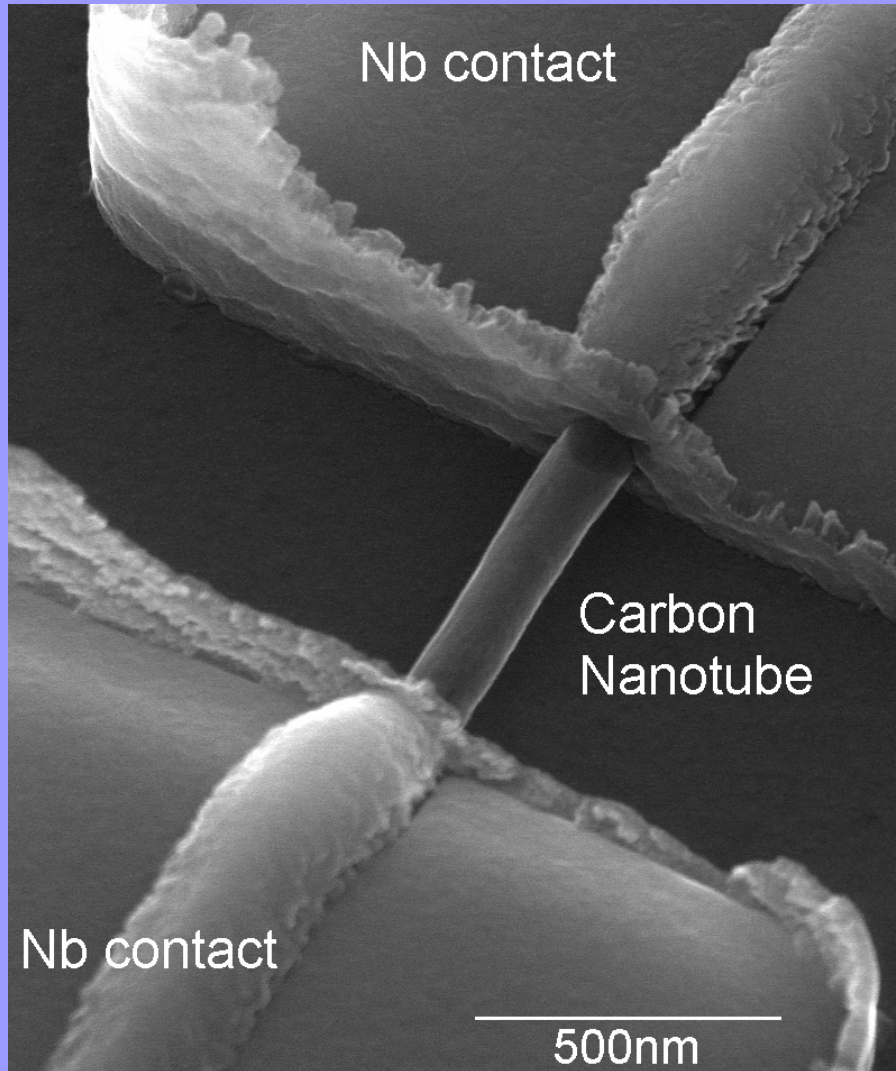
Problems to overcome

- Back-end processes – so need to limit growth to ~450 C not 600C
- So major need to improve quality of 450C PECVD MWNT
- For 2 micron via CNTs resistance is about 5 Ω - currently about two orders higher than Cu and 1 order higher than W
- Contacts to interconnects/packing density/diameter of tubes
- Currently 10^{10}cm^{-2} - aiming for 10^{12}cm^{-2}

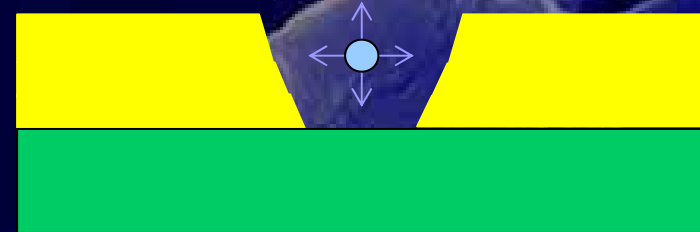
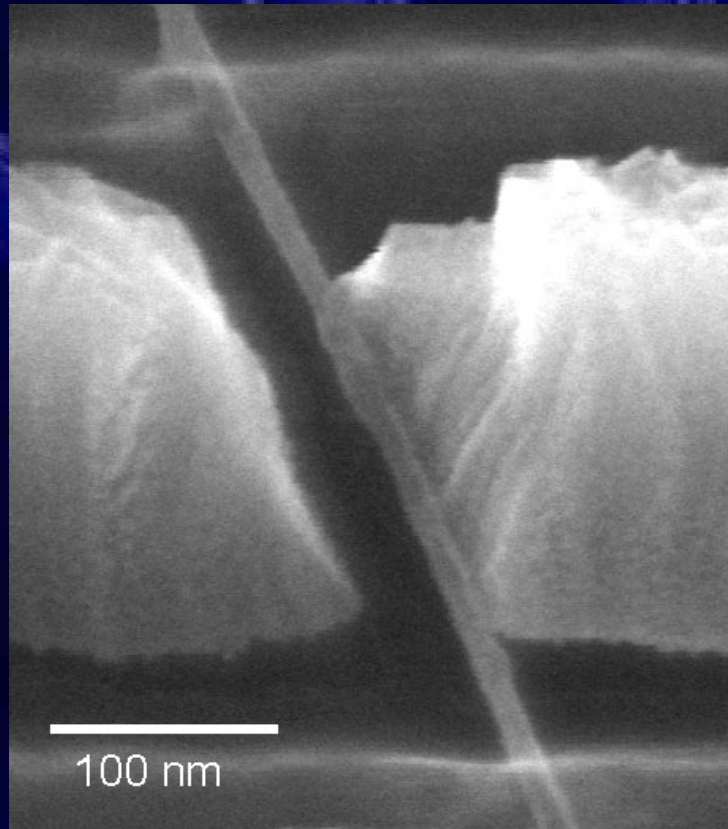
Possible ITO replacement for Flexible Displays (Eikos)



MEMS/NEMS



Possible application - Oscillator



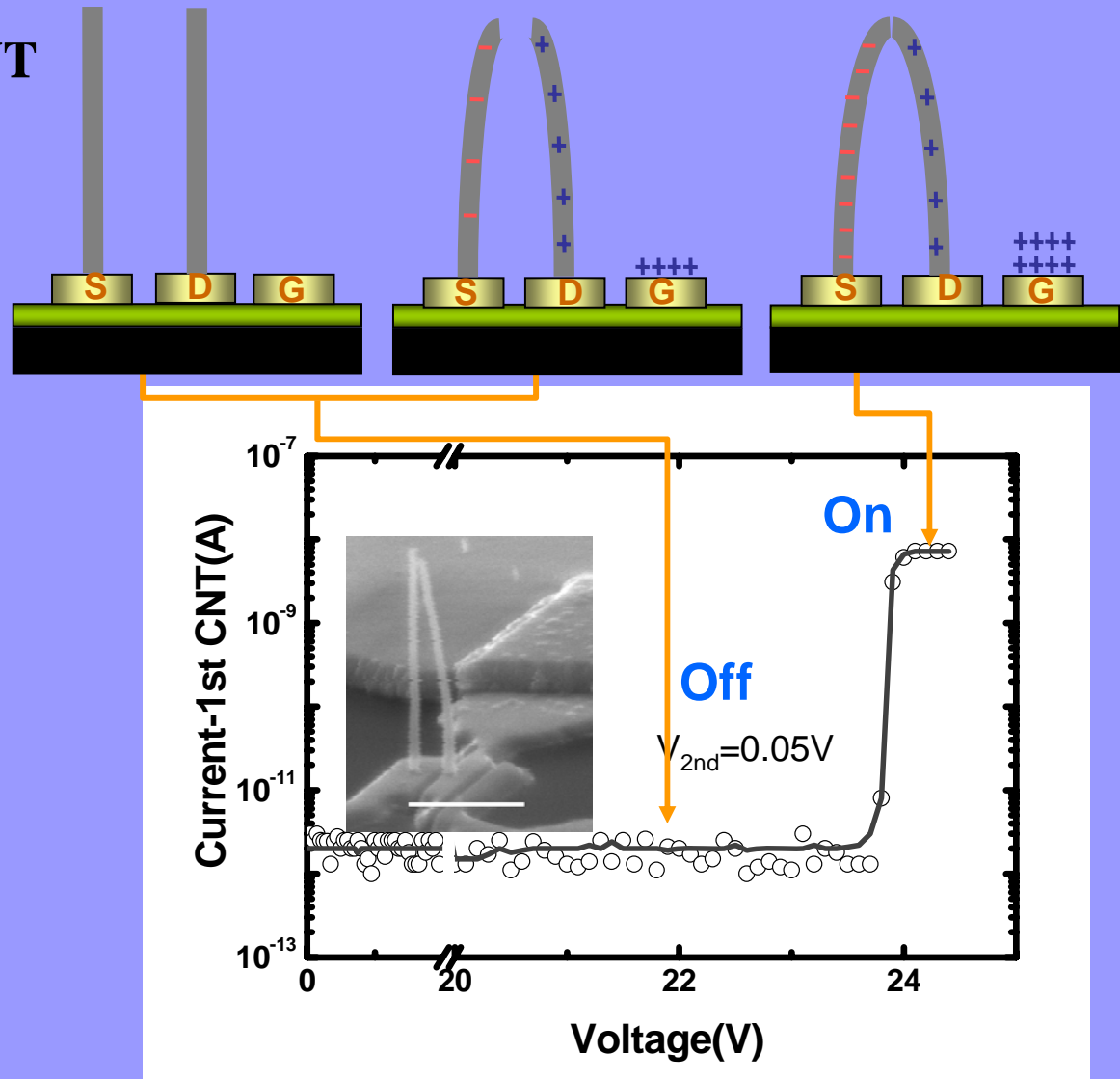
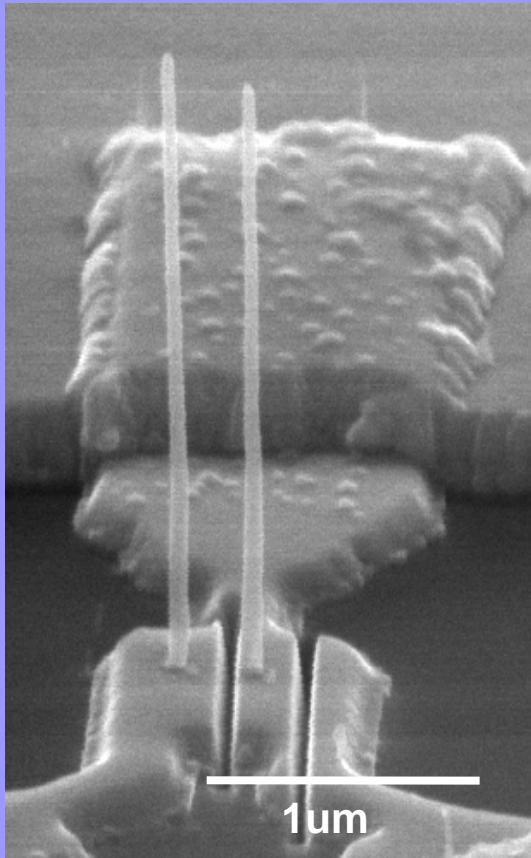
- Nano-electromechanical Oscillator

$$f_o \sim \frac{\{E_b(D_o^2 + D_i^2)\}^{1/2}}{L} \geq 5 \text{ GHz}$$

D_o, D_i : outer & inner diameters
 L : suspended nanotube length
 E_b : Young's modulus, ρ : density

- The high side gate electrodes balances the van der Waals force enabling nanotubes to remain suspended.

- NEM switch with MWCNT



- On & Off state is very clear ; mechanical movement of CNT
- MWCNTs did not return to original position without applied biases

SENSORS

As grown CNTs are hydrophobic but by means of various processes (electrochemical,thermal etc) they can be made hydrophilic. Such hydrophilic CNTs can effectively immobilize antibody which can e.g allow specific bacteria to attach.

Functionalisation of CNTs make them useful as DNA detectors at the sub-attomole level



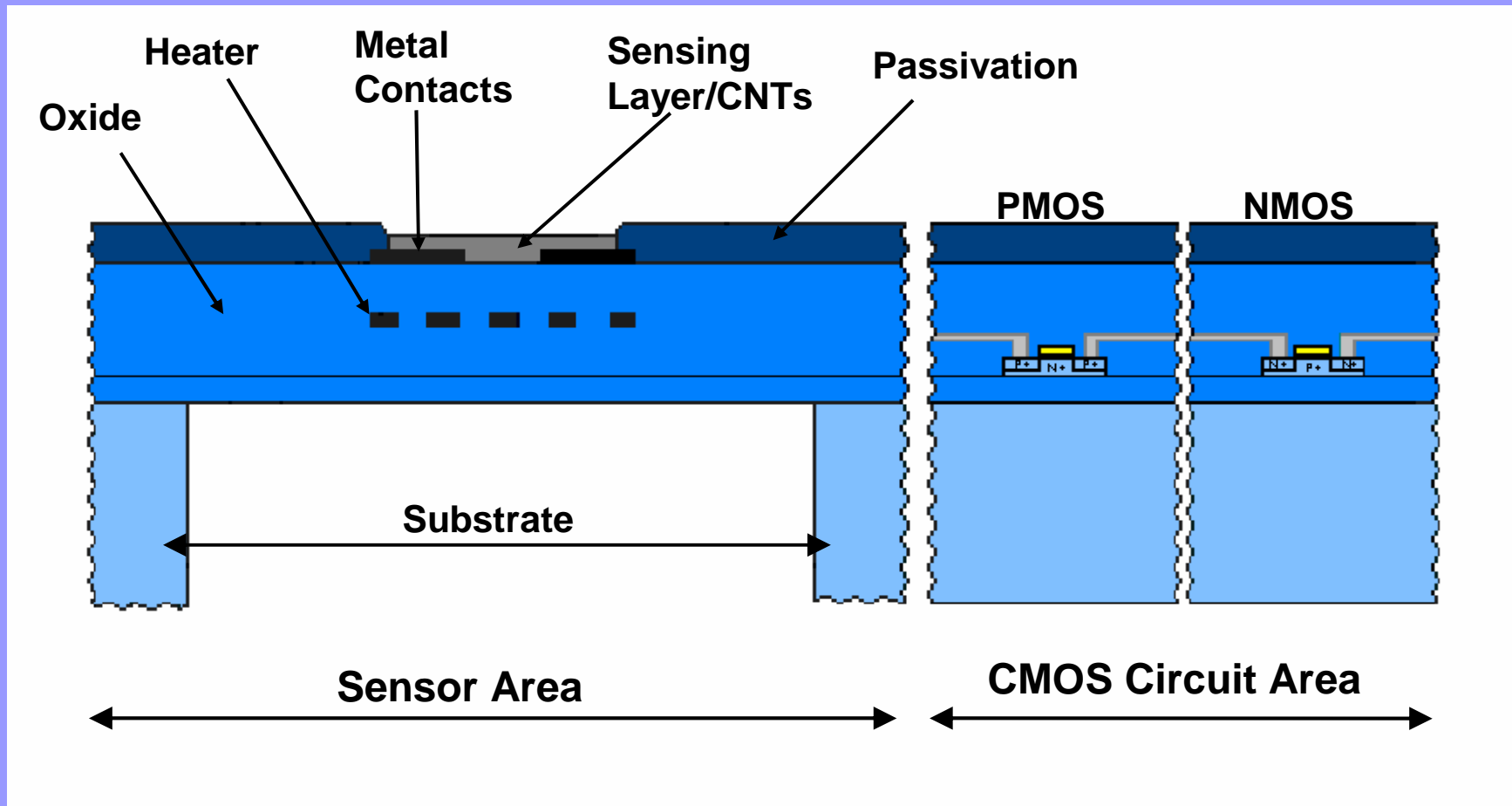


How CNTs may work as gas sensors

- Chemical sensors based on SWCNTs have also been demonstrated- upon exposure to NO_2 or NH_3 the electrical resistance of semiconducting SWCNTs is seen to dramatically alter- v.fast response time
- CNTs that are grown are generally p-type.
- Gases like NO_2 are electrophillic so it can remove electrons from CNTs
- CNT conduction increases and therefore the resistance of the film decreases.

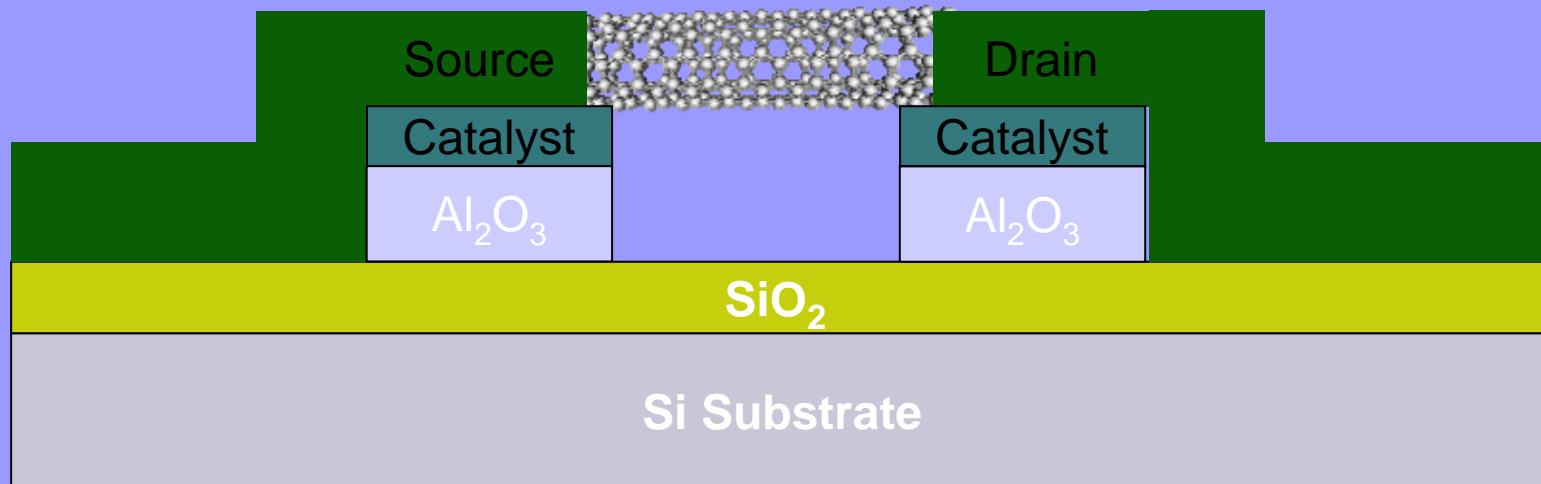


Proposed SOI/CNT Structure



Transistors

Bottom gate transistor fabrication



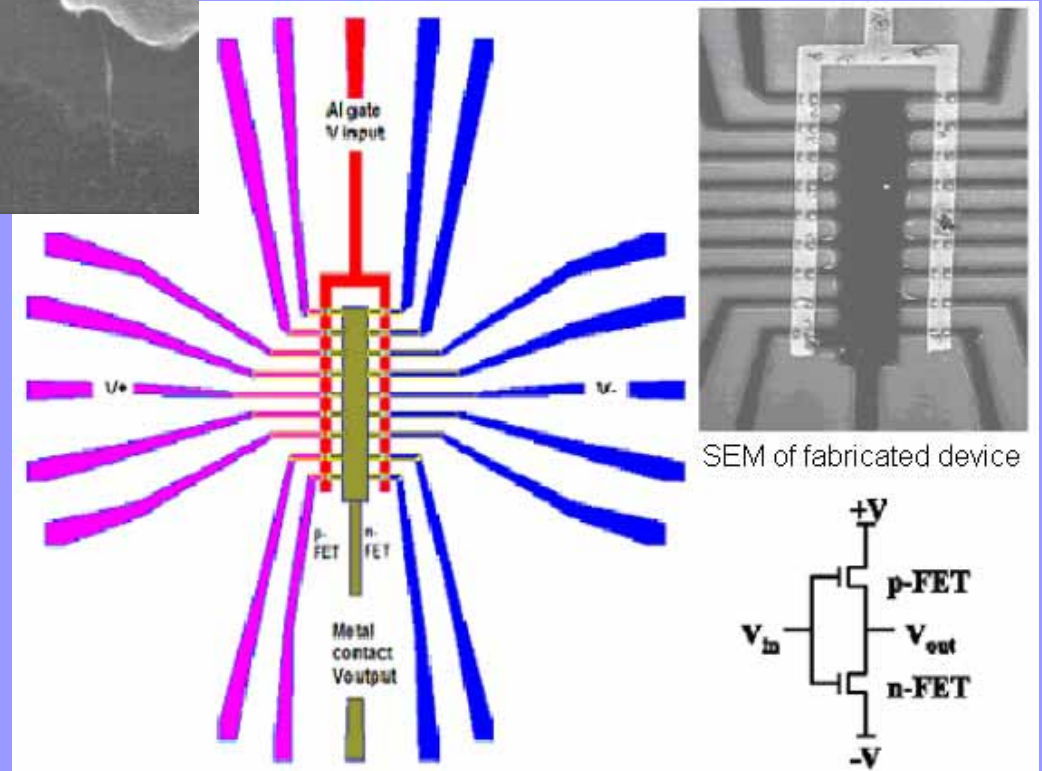
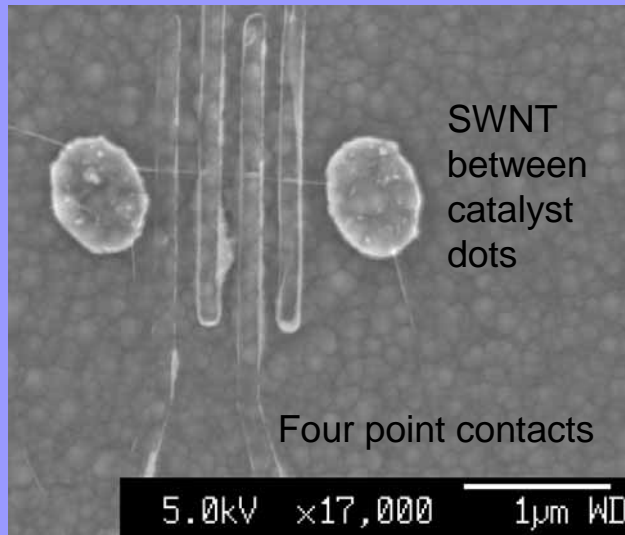
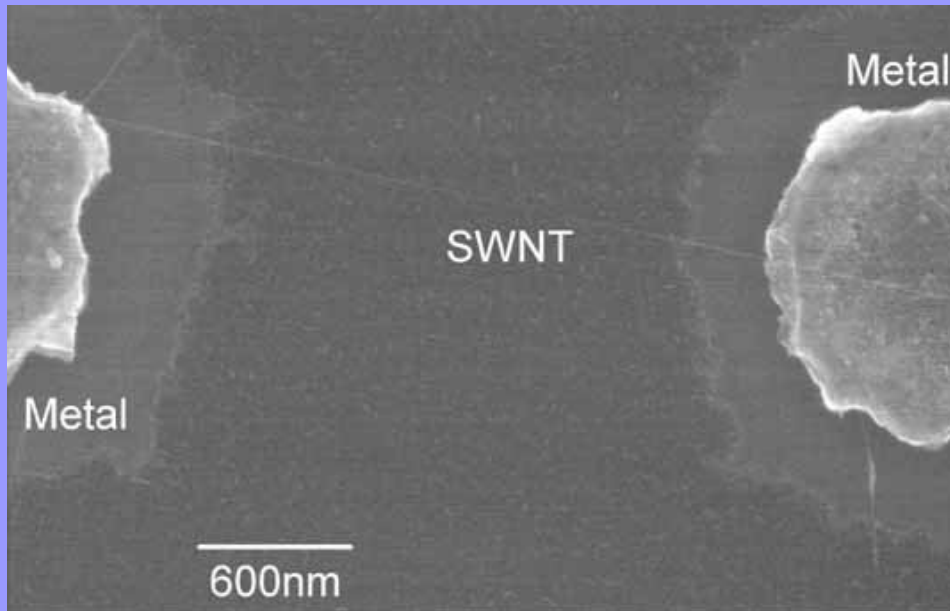
- Concept is to place catalyst dots at **known locations**
- **Dots size and distance** are controlled to ensure high yield of SWCNT bridges.
- Only SWCNT which bridge dots are contacted – the rest grow to the SiO₂ substrate

Direct SWNT

growth

between contacts

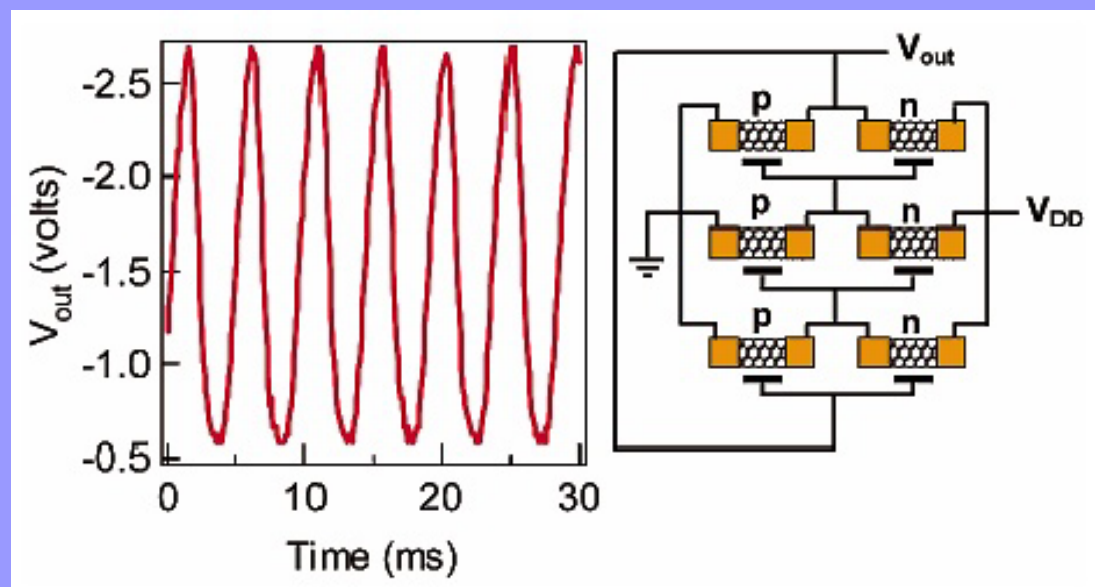
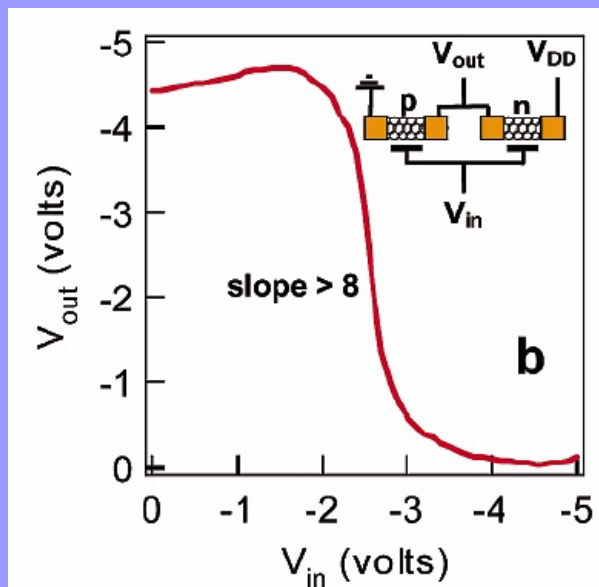
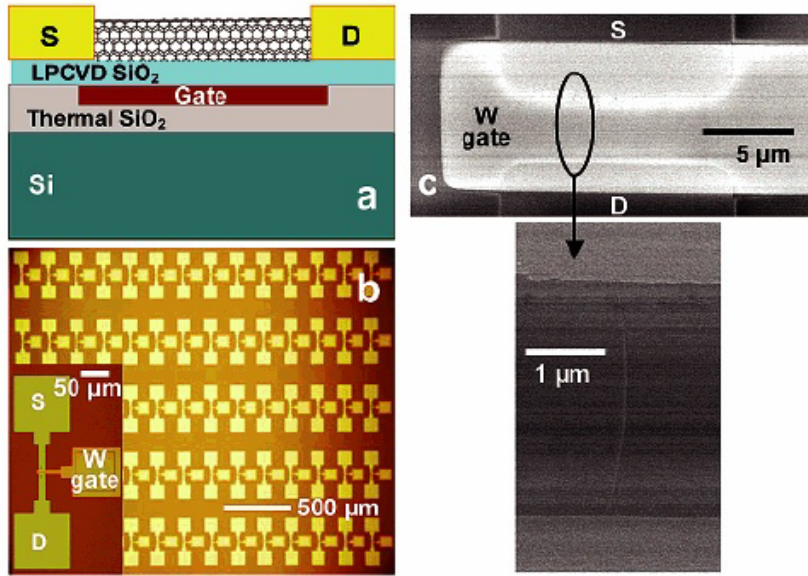
CNT-based logic fabrication



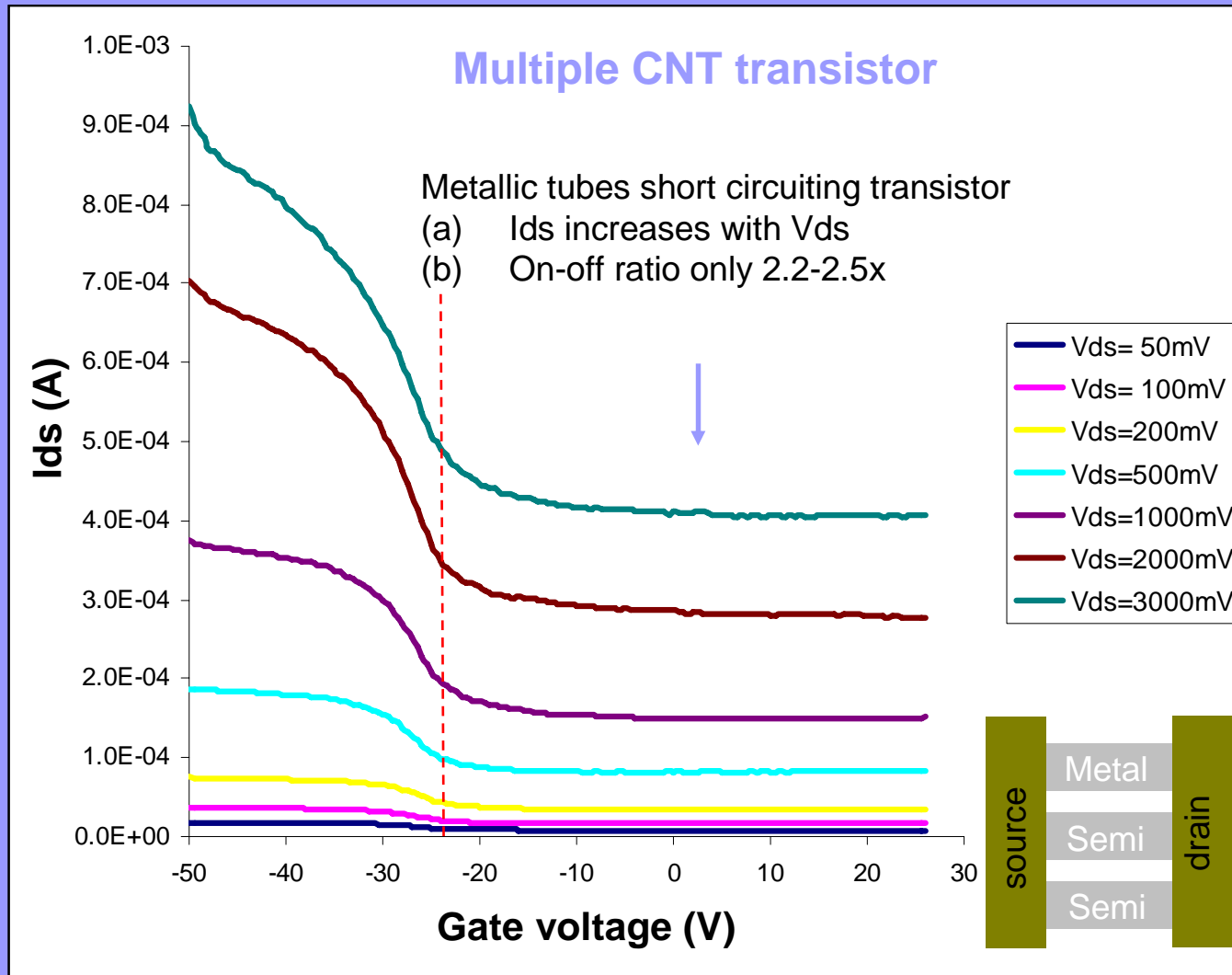
Logic with CNT

- Simple integration and logic functions demonstrated

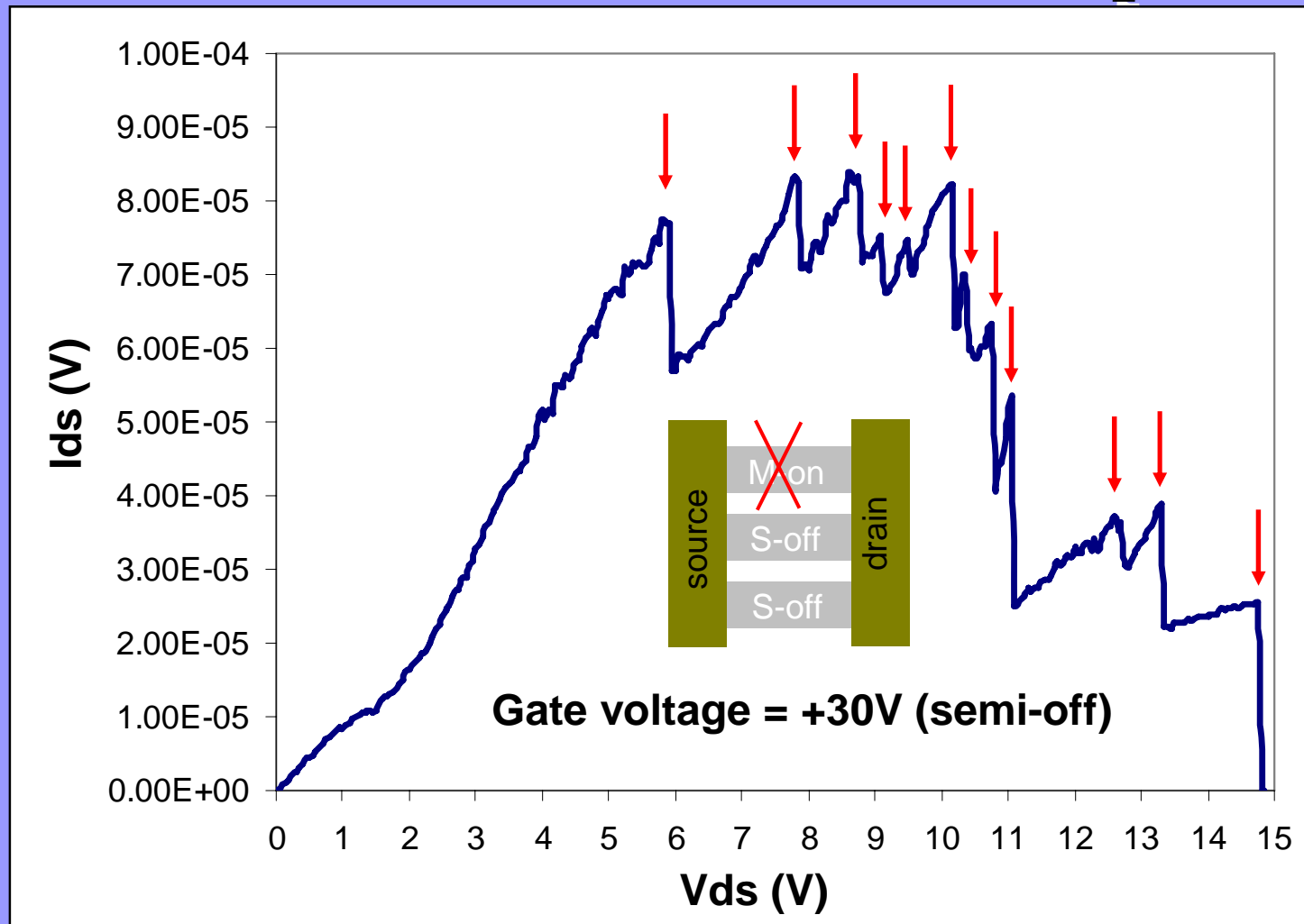
[Javey et al, Nanoletters 2, 929 (2002)]



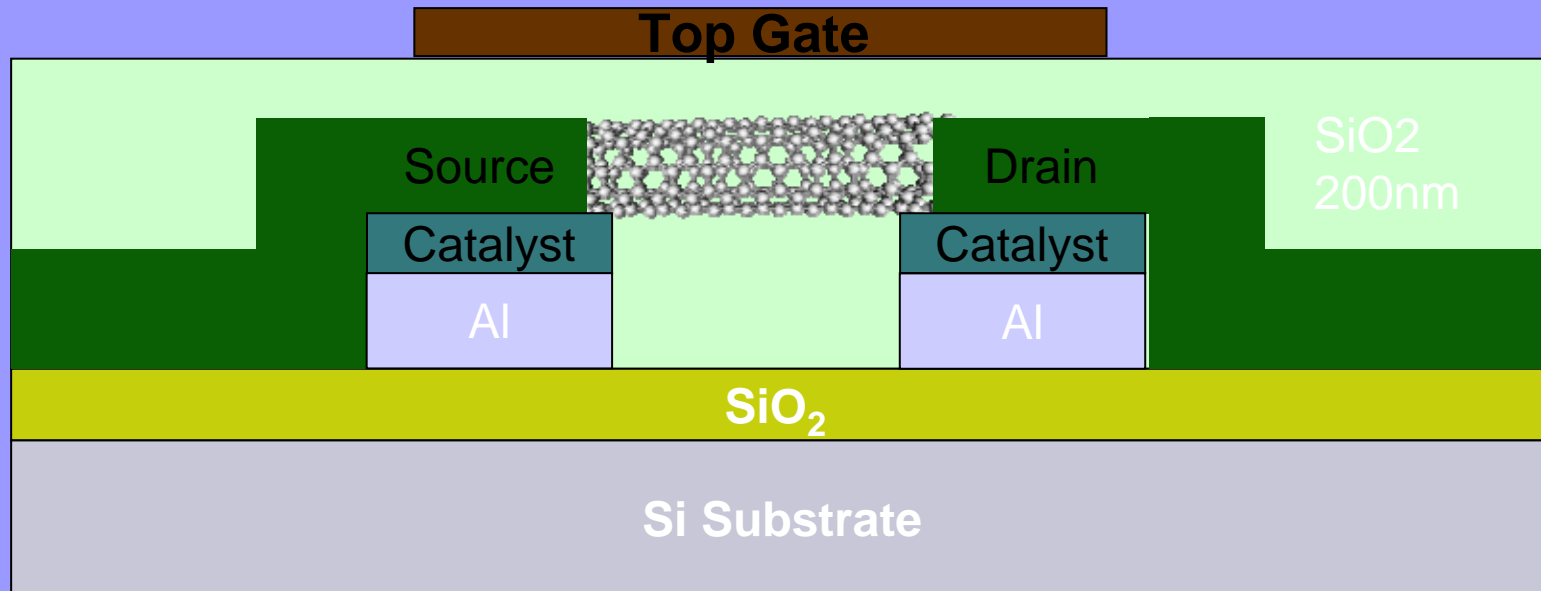
Bottom Gate Transistor Characteristics



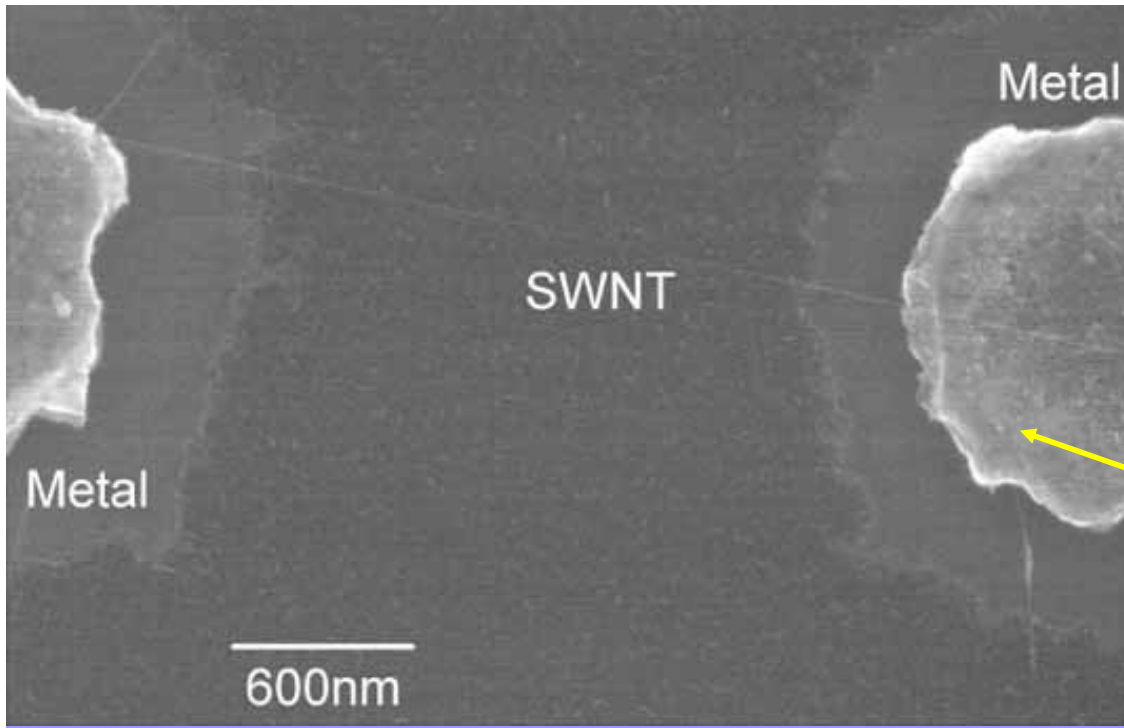
Burn-off metallic SWNTs [IBM]



Top gate transistor fabrication

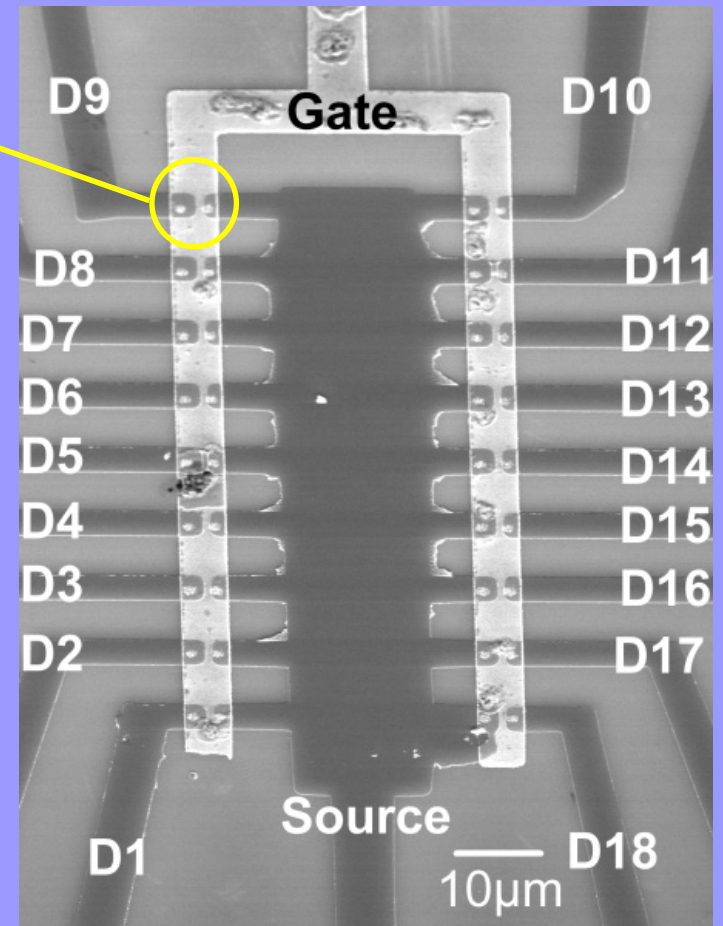


- Concept is to place catalyst dots at **known locations**
- **Dots size and distance** are controlled to ensure high yield of SWCNT bridges.
- Only SWCNT which bridge dots are contacted – the rest grow to the SiO₂ substrate

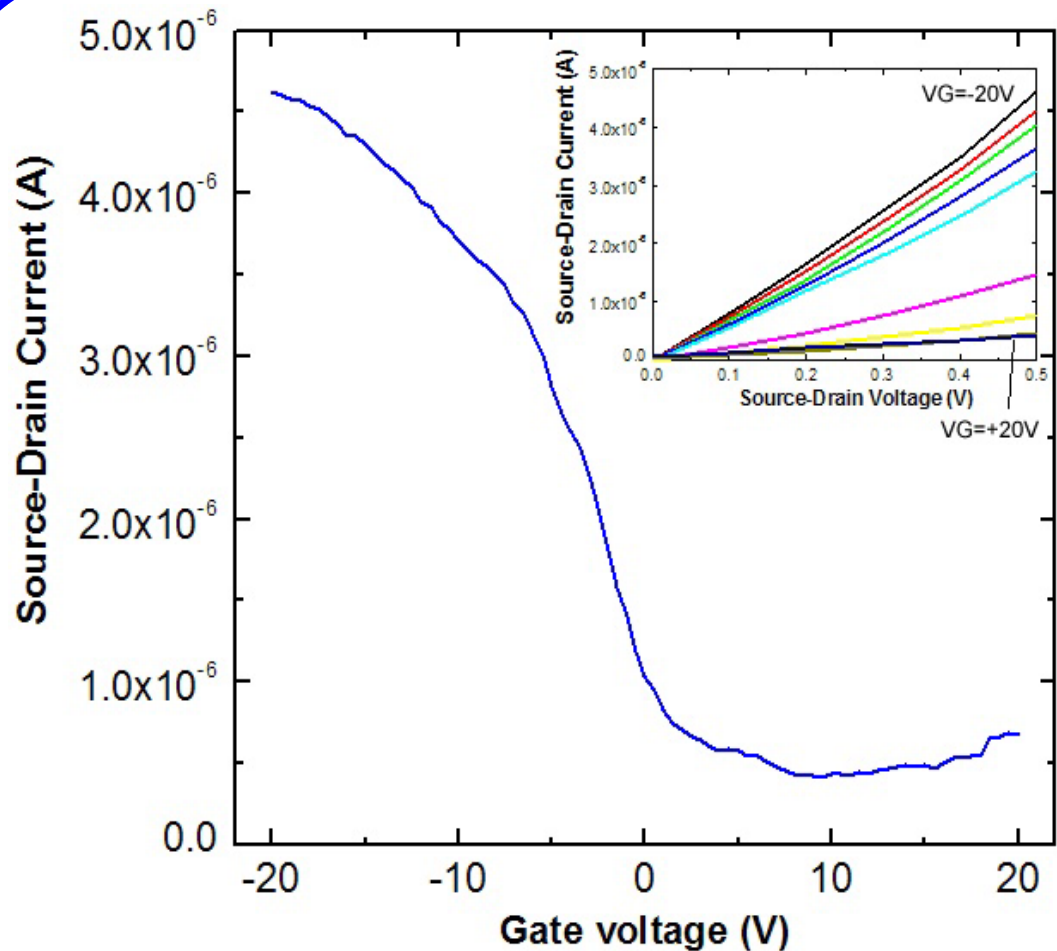


SEM Images of Devices

- ~ 1-3 SWCNT bridging for 1 μ m dots
- CNT's not bridging grow towards the SiO₂ and are not contacted



Typical Top Gate Transistor Characteristics



- P-type FET response
- On-off $\sim 5-10$
- Needs to be pre-burned before top gate fabrication
- Yield 16/18

Conclusions

- Growth of SWCNTs and MWCNTs easy using a variety of methodologies
- Near Term applications dominated by Field Emission properties
- Longer Term applications are many and varied BUT
- Control of Chirality and position vital for further development

Thank you for your attention!

Acknowledgements for funding:



EPSRC CBE
Initiative

Advance
Nanotech

Samsung

FEI

Thales