Carbon Nanotubes for Data Processing

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Based on pages 473-497 of “Nanoelectronics and Information Technology”, Rainer Waser

Introduction

- Carbon nanotubes (CNTs) discovered by Iijma (NEC Labs), 1991
- CNT can be thought of as a stripe cut from a single graphite plane (Graphene) and rolled up to a hollow seamless cylinder (fig1)

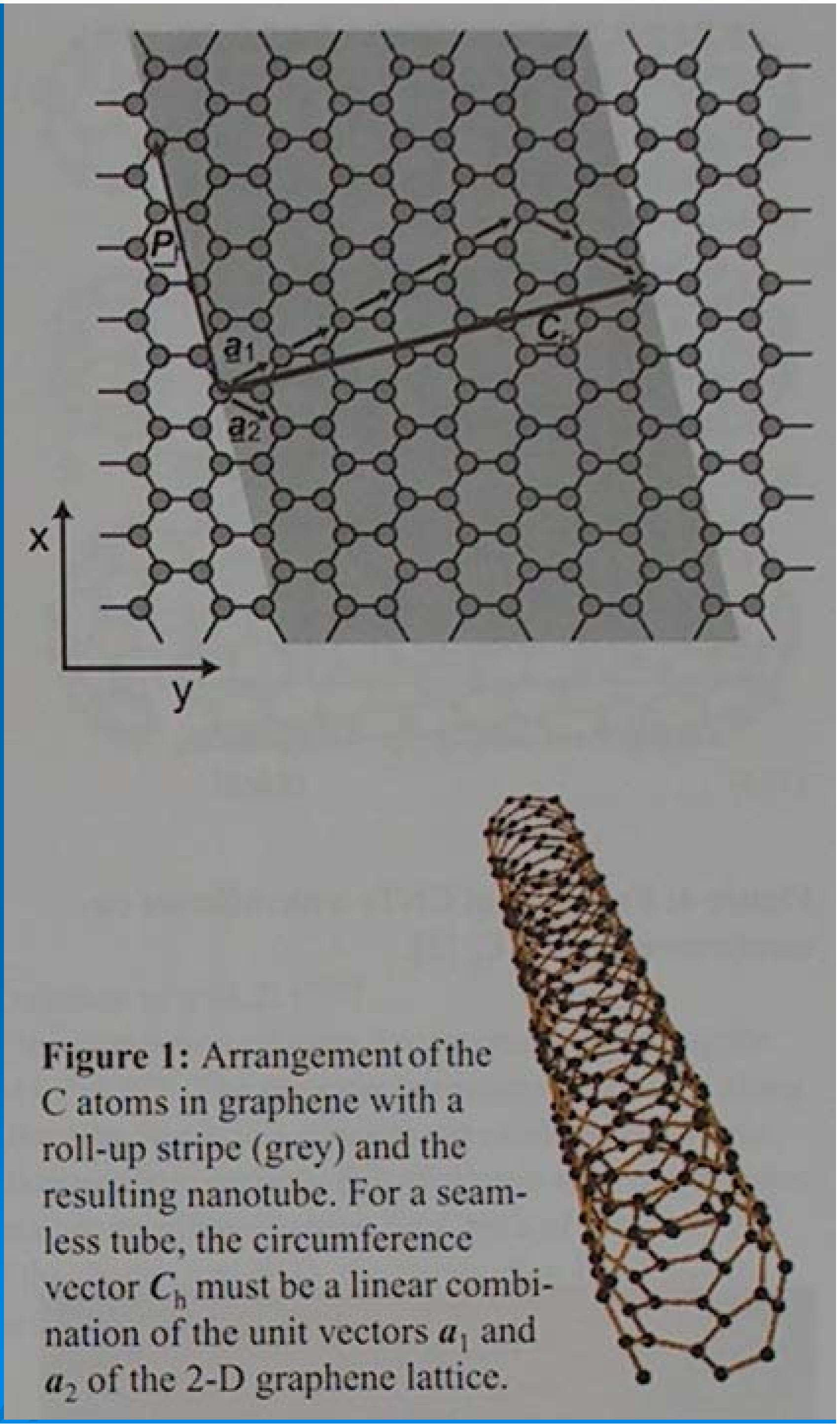


Figure 1: Arrangement of the C atoms in graphene with a roll-up stripe (grey) and the resulting nanotube. For a seamless tube, the circumference vector C_h must be a linear combination of the unit vectors a_1 and a_2 of the 2-D graphene lattice.

Introduction

- C atoms form a hexagonal network, because of their sp^2 hybridization
- Small contributions of sp^3 are mixed in, due to the curvature of the network in case of CNTs
- CNT diameters between 1 and 10 nm and micrometers long have been fabricated

Introduction

- CNT ends may be open or capped with half a fullerene molecule
- Two main categories are Single Wall Nanotubes (SWNTs) and Multi Wall Nanotubes (MWNTs) (fig2)

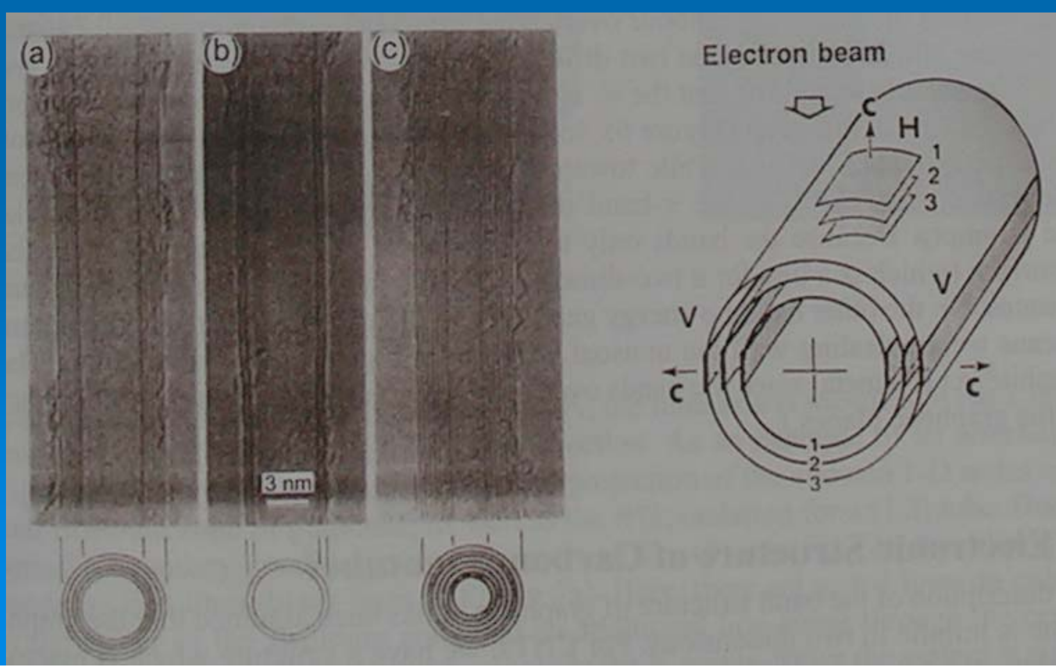


Figure 2: TEM image and imaging scheme of multi-wall nanotubes with various inner and outer diameters, d_i and d_o, and numbers of cyclindrical shells N reported by Iijima [1]:
(a) $N = 5$, $d_o = 6.7$ nm,
(b) $N = 2$, $d_o = 5.5$ nm,
(c) $N = 7$, $d_i = 2.3$ nm, $d_o = 6.5$ nm.

Introduction

- Ropes of CNTs are frequently encountered which are self-assembled bundles of SWNTs (fig 3)
- The small size of CNTs and their transport properties are very attractive for future electronic applications

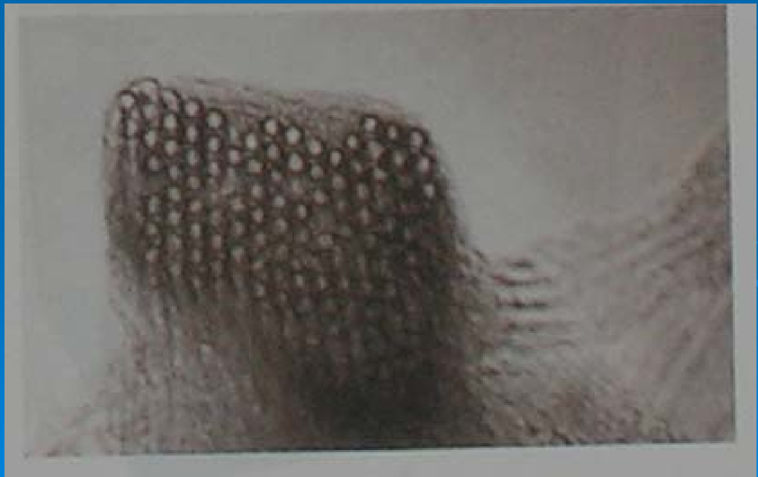


Figure 3: TEM cross section of a robe of SWNTs illustrating a hexagonal (i. e. densely packed) arrangement of the aligned tubes [4], [5].

Electronic Properties

- Geometrical structure
  - The structure of CNTs is described by the circumference or chiral vector, C_h, defined by:

    $$C_h = na1 + ma2$$
  - Where a1 and a2 are unit vectors in the hexagonal lattice (see fig 1)
  - C_h also defines P_h , periodicity of the tube parallel to the tube axis
  - It also settles the chiral angle which is the angle between C_h and a1

Electronic Properties

- m=n=0 : chiral angle is zero; tube is called zig-zag
- m=n : chiral angle is 30; tube is called arm-chair
- Other tubes are called chiral and have angles between 0 and 30
- Figure (fig 4 ,5) shows these three structures and STM image of a SWNT

Electronic Properties

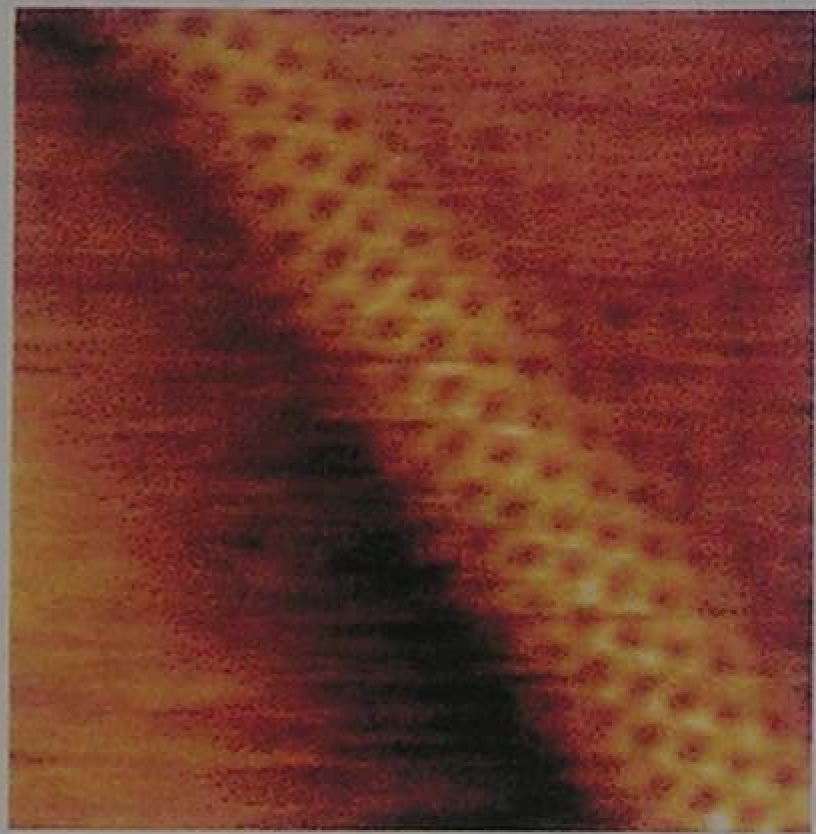


Figure 5: STM image at 77 K of a SWNT at the surface of a rope [6].

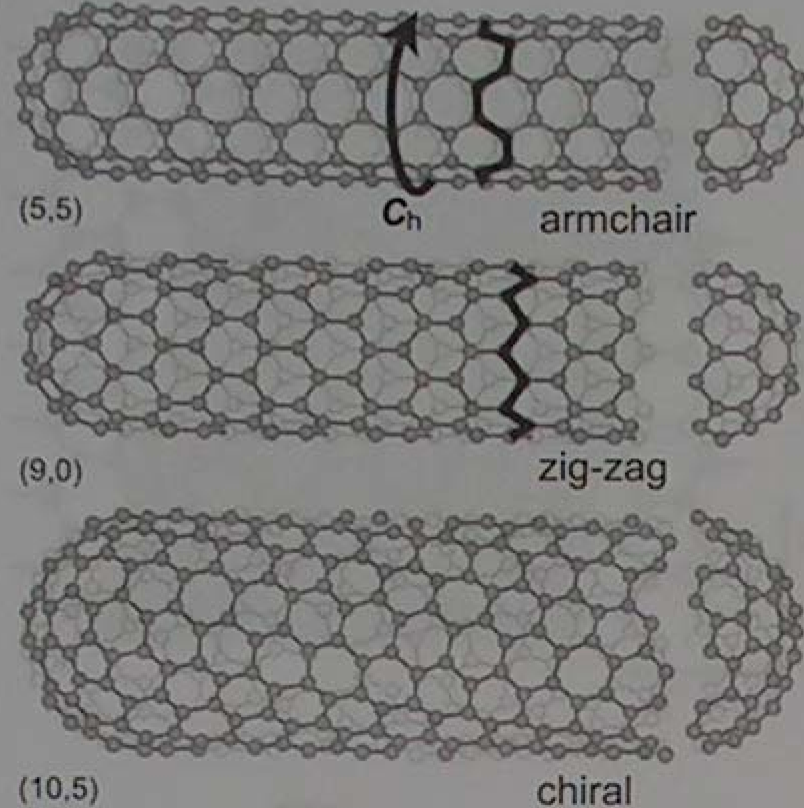


Figure 4: Examples of CNTs with different circumference vectors C_h [5].

Electronic properties

- Electronic structure of Graphene
  - In graphene, a bonding π-band and an anti-binding π*-band is formed
  - Wallace derived an expression for the 2-D energy sates, W2D, of the π electrons as a function of wave vectors k_x,k_y :

$$W_{2D}(k_x,k_y) = \pm\gamma_0[1+4\cos(\frac{\sqrt{3}k_x a}{2})\cos(\frac{k_y a}{2})+4\cos^2(\frac{k_y a}{2})]^{1/2}$$

  - γ0 denotes nearest neighbor overlap integral and a=0.246 nm is the in plane lattice constant
  - The two signs in the relation represent π and π*-band

Electronic Structure of Graphene

- Figure (fig 6) shows that π and π*-band just touch each other at the corners of the 2-D Brillouin zone

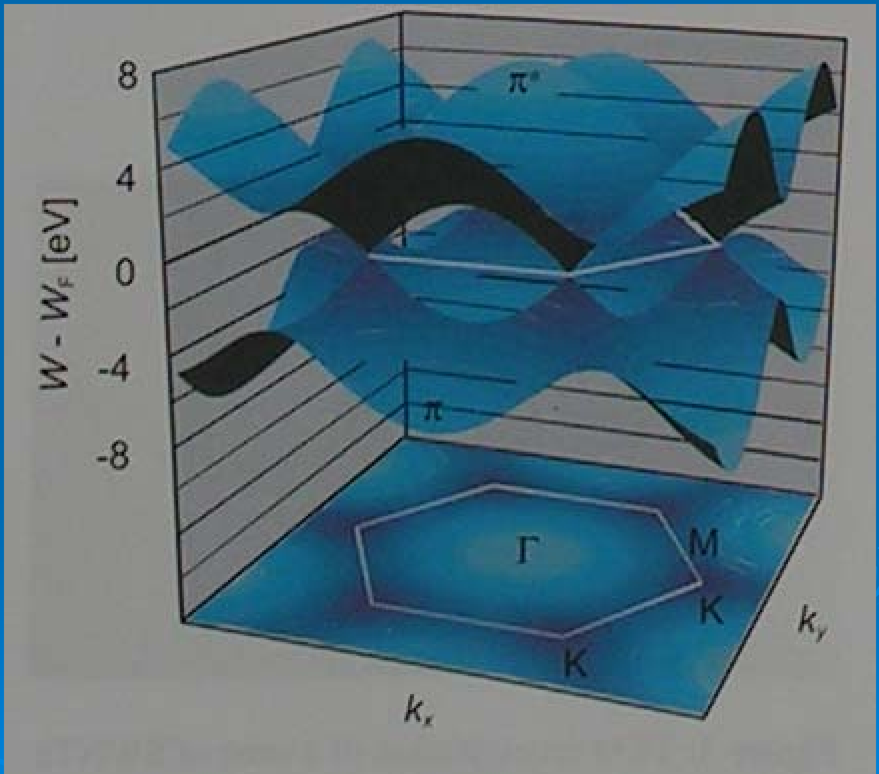


Figure 6: 3-D illustration of the dispersion relation of graphene.

Electronic Structure of Graphene

- In the vicinity of Γ point, the dispersion relation is parabolically shaped, while towards the corners (K points) it shows a linear dependence on W(k)
- No energy gap exist in the graphene dispersion relation, we are dealing with a gapless semiconductor
- Real graphite is a metal and the bands overlap by 40 meV due to interaction of graphene planes

Electronic Structure of Carbon Nanotubes

- For CNTs, the structure is macroscopic along the tube axis, but the circumference is in atomic scale
- Density of allowed quantum mechanical states in axial direction will be high, but the number of states in circumferential direction will be limited
- Periodic boundary conditions will define allowed modes (1-D states) along the tube axis according to:

$$C_h.k = 2\pi j \text{ with } j = 0,1,2,\ldots$$

For arm-chair tubes, allowed values for circumferential direction are (based on periodic boundary conditions)

$$k_{y,j} = \frac{j}{q_y}\frac{2\pi}{\sqrt{3}a}, \mathrm{q_y} = m = n$$

Electronic Structure of Carbon Nanotubes

- Figure (fig 7) shows dispersion relation, the projection of allowed 1-D states onto the first Brillouin zone of graphene and W(kx) relation for a (3,3) tube

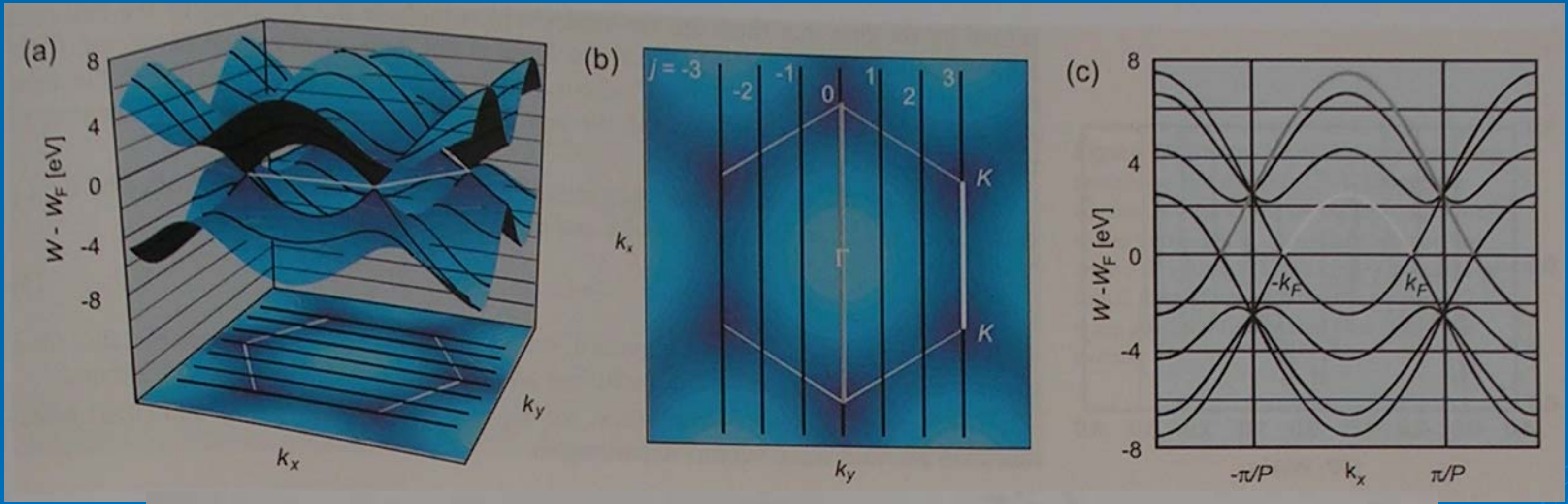


Figure 7: Dispersion relation of a (3,3) CNT.
(a) 3-D illustration of the dispersion relation for graphene including the allowed states for the (3,3) CNT. The periodic boundary conditions along the circumference of the tube result in a discrete set of allowed k_y values.
(b) Projection of the allowed states onto the first Brillouin zone of graphene. Obviously, the K points are allowed states for CNTs of this chirality.
(c) 2-D illustration of the dispersion $W(k_x)$. The states at the Fermi level indicate the metallic behaviour of this tube. The periodicity volume in the k-space is given by the interval from $-\pi/P$ to $+\pi/P$.

Electronic Structure of Carbon Nanotubes

- Allowed states condense into lines (there are qy=3 lines on either side of the center of the Brillouin zone)
- In case of (3,3) tube (and all other arm-chair tubes), the allowed states (lines) include the K points of Brillouin zone of graphene, hence all arm-chair tubes show a metallic behavior

Electronic Structure of Carbon Nanotubes

- Figure (fig 8) shows the dispersion relation, the projection of allowed 1-D states onto Brillouin zone of graphene and the W(kx) relation for a chiral (4,2) tube

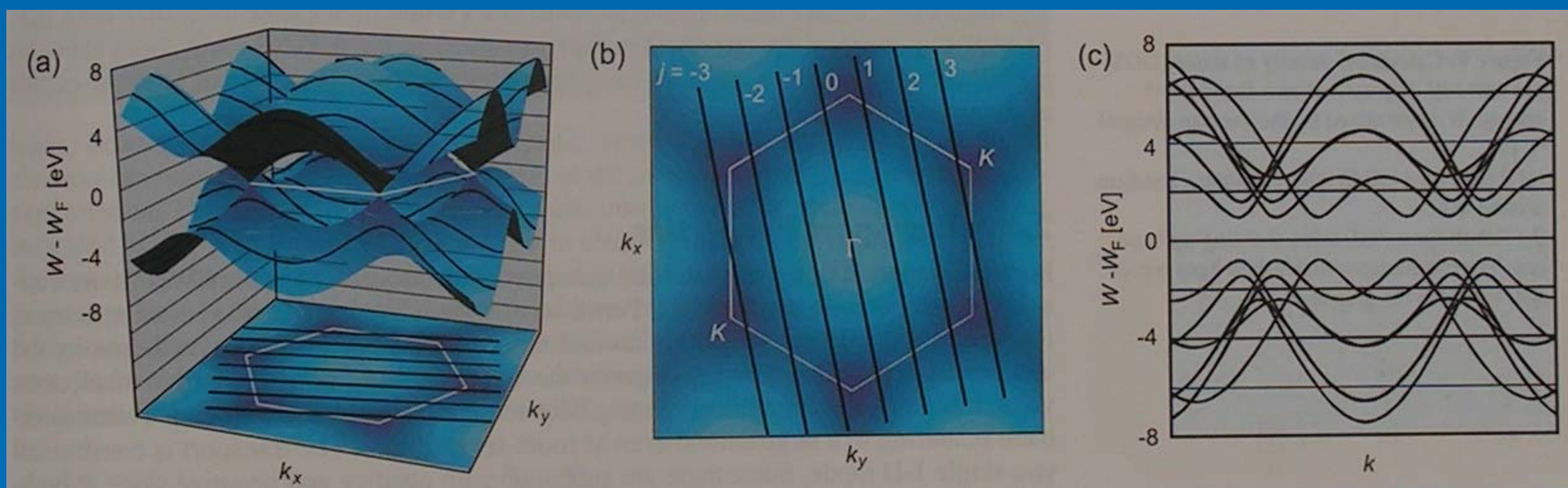


Figure 8: Dispersion relation of a (4,2) CNT.
(a) 3-D illustration of the dispersion relation for graphene including the allowed states for the (4,2) CNT. The periodic boundary conditions along the circumference of the tube result in a discrete set of allowed k values.
(b) Projection of the allowed states onto the first Brillouin zone of graphene. Obviously, the K points are no allowed states for CNTs of this chirality.
(c) 2-D illustration of the dispersion $W(k)$. the conduction band and the valence band are separated by a bandgap.

Electronic Structure of Carbon Nanotubes

- Ch vector is not parallel to y direction and there is a mixed quantization of kx and ky
- There are no modes which include the K points of the Brillouin zone of graphene, WF is now in a bandgap, therefore, this type of tube is semiconductor with bandgap of few eV
- In general, bandgap decreases with increasing diameter of the tube

Electronic Structure of Carbon Nanotubes

- Metallic or semiconducting behavior of CNTs is determined by Ch vector and relation between n and m
- **Metallic behavior occurs for n-m =3q tubes**
- For and ideal scattering free (ballistic) transport of a metallic CNT, one expects (Landauer) conductance:

$$G = 2.2.\frac{e^2}{h} = \frac{4e^2}{h}$$

Electronic Structure of Carbon Nanotubes

- It is expected that ballistic transport properties are maintained over several micrometers, for transport in larger scale, scattering has to be taken into account
- The two terminal resistance of a CNT of length L will be:

$$R_{imp} = \frac{h}{4e^2} . \frac{L}{\lambda_{imp}}, \lambda_{\mathrm{imp}} : \text{elastic mean free path, roughly the average distance between impurity centers}$$

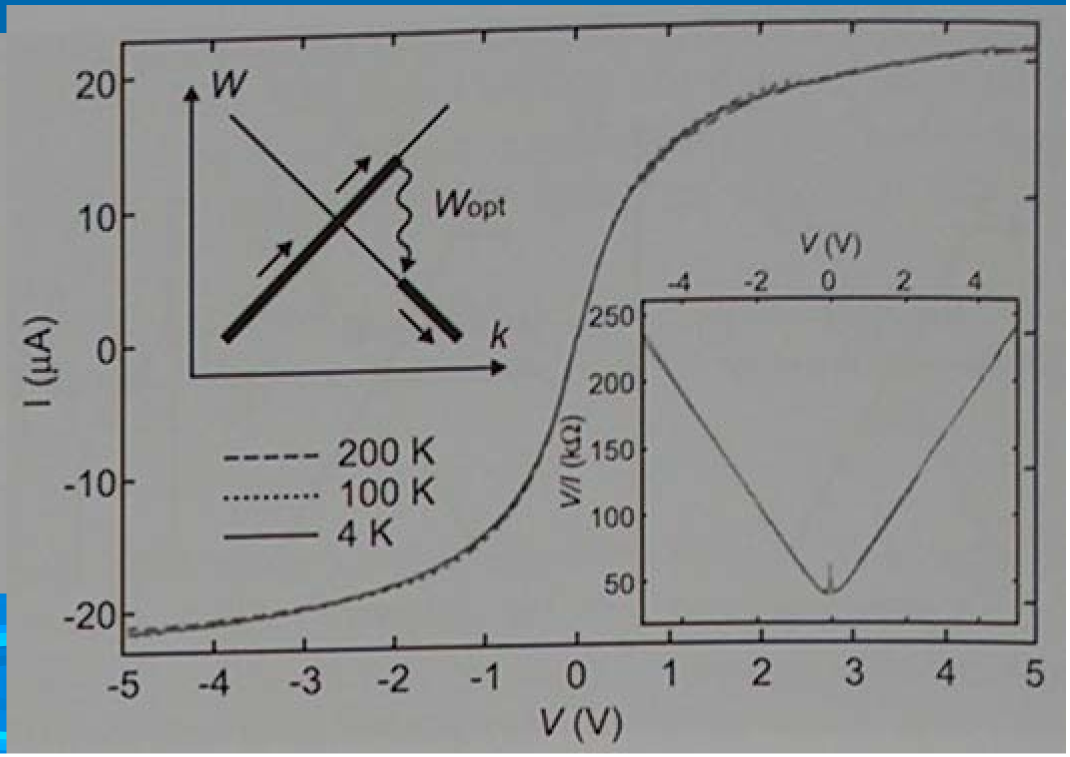
Transport properties

- Experimental and theoretical results have shown that intertube coupling within MWNTs and ropes of SWNTs have a relatively small effect on band structure of a tube,
- Hence, metallic or semiconducting tubes retain their properties if they are part of a MWNT or a rope

Transport properties

- Figure (fig 12) shows the I-V characteristics of a metallic CNT for different temperatures
- For v<0.2, I-V is linear, for larger voltages, I-V is strongly non-linear, inset shows the resistance
- This is mainly due to phonon scattering phenomena

Figure 12: High-field *I-V* characteristics for metallic CNTs at different temperatures. The right inset plots $V/I = R$ vs. V. The left inset shows a section of the dispersion relation and illustrates the phonon emission [14].



Contacts

- It is essential to provide some kind of contact between nanotube and outside world
- One way is to locate the tube on the substrate by SEM and then design the desired contact by electron beam lithography, metal deposition and lift-off,
- Figure (fig 14) shows an example

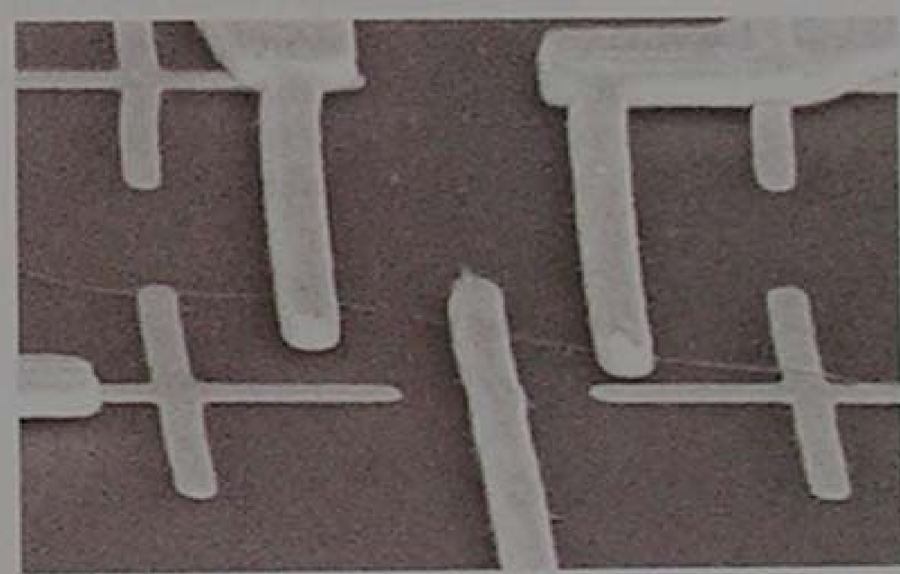


Figure 14: SEM image of a rope of single-wall nanotubes contacted by several gold fingers attached to the top of the tube.

Contacts

- It is hard to make a highly transmissive, minimum invasive contact
- Contacts connected to metallic CNTs can cause severe backscattering
- Contacting semiconducting CNTs to metal is more complicated
- One would in general expect a Schottkey barrier in semiconductor nanotube/metal interface

Contacts

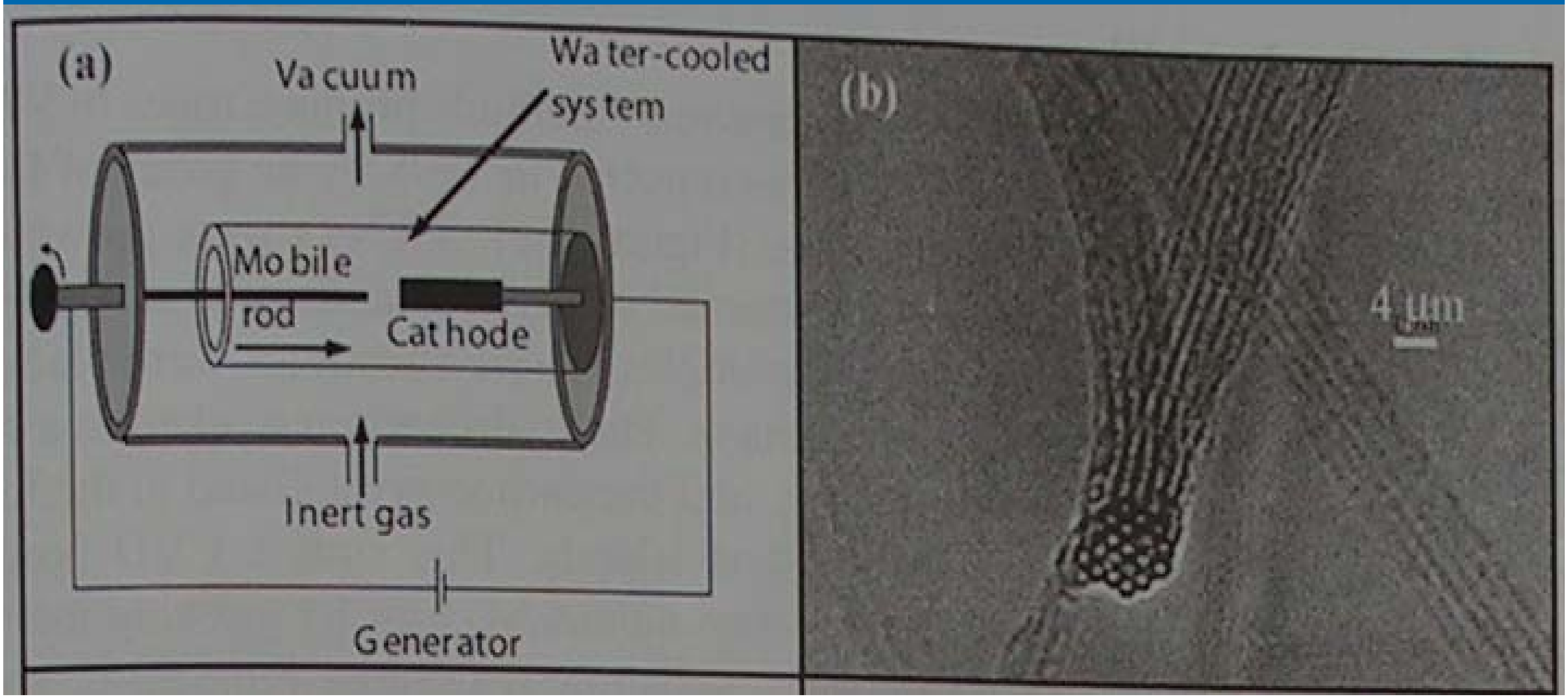
- Barrier height would change by the work function difference between metal and CNT
- Metals with high work functions reduce the barrier and facilitate hole injection into the CNT
- Further research is required to reveal the nature of carbon nanotube/metal contacts

Synthesis of Carbon nanotubes

- Synthetic methods
  - Electric arc discharge
    - First MWNTs were fabricated with arc discharge method
    - The method consists of applying a voltage between two graphite electrodes held close together in a chamber filled with an inert gas
    - Carbon evaporates and crystallizes on the end of negative electrode forming MWNTs

Synthesis of Carbon nanotubes

- Introduction of small amounts of transition metals like Fe, Co and Ni leads to formation of SWNTs, Figure (fig 15a,b)

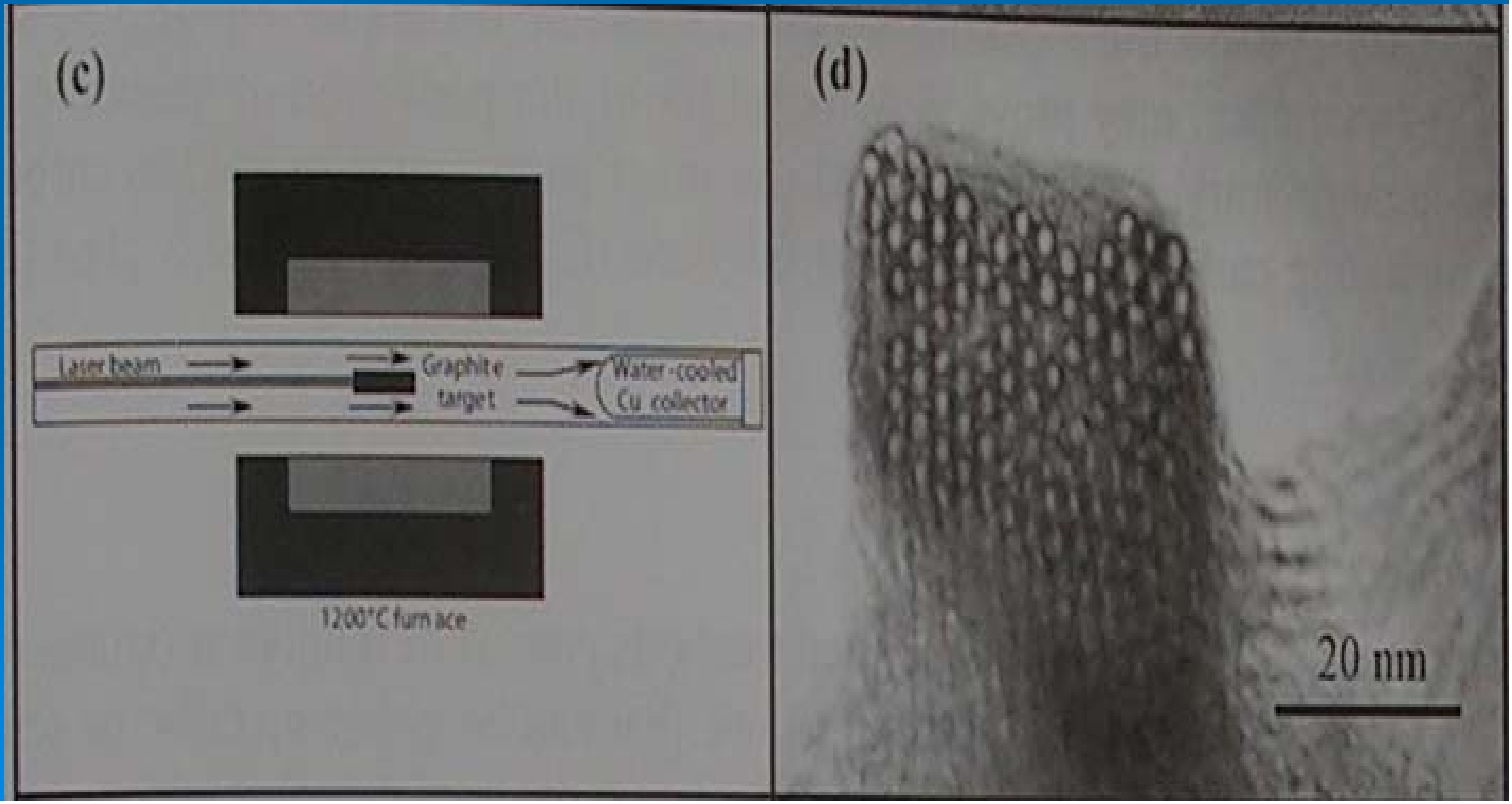


Synthesis of Carbon nanotubes

- Laser vaporization
  - High yield, large scale production of SWNTs
  - A target of graphite containing small amounts of Ni and Co powder is placed in the middle of a tube furnace and hit by a series of laser pulses
  - Tubes are formed as packed ropes of 100 to 500 parallel SWNTs

Synthesis of Carbon nanotubes

- Large amounts of SWNTs can be made based on this method, Figure (fig 15c,d)

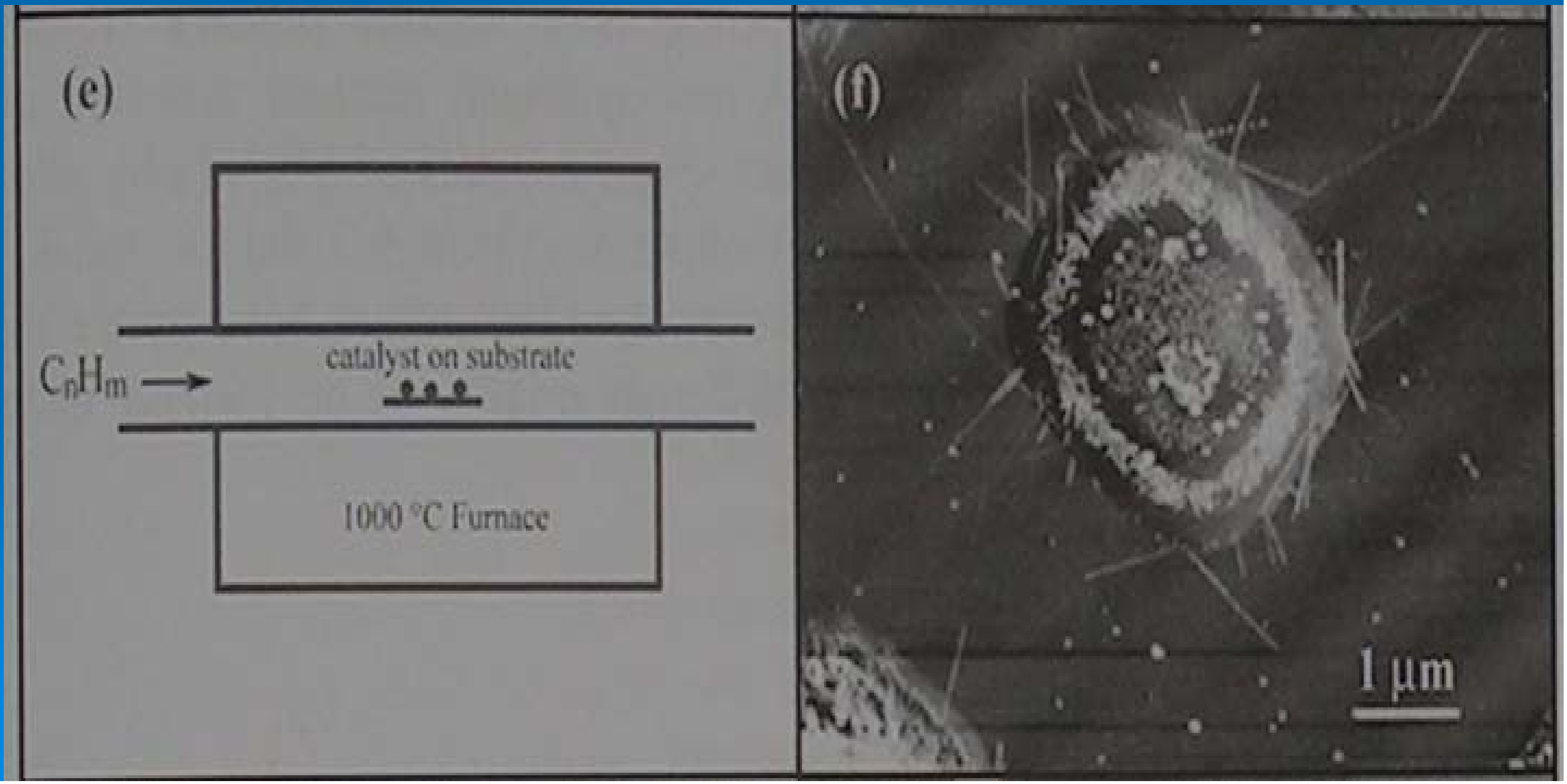


Synthesis of Carbon nanotubes

- Chemical vapor depostion
  - Production method for single SWNTs
  - Lithographically patterned islands of alumina (Al_2O_3) powders containing Fe and Mo catalytic nanoparticles
  - Substrates were places in a furnace at 1000 c, under flow of methane

Synthesis of Carbon nanotubes

- Useful for in situ production of nanotube assembelies and nanocircuitry, Figure (fig 15e,f)

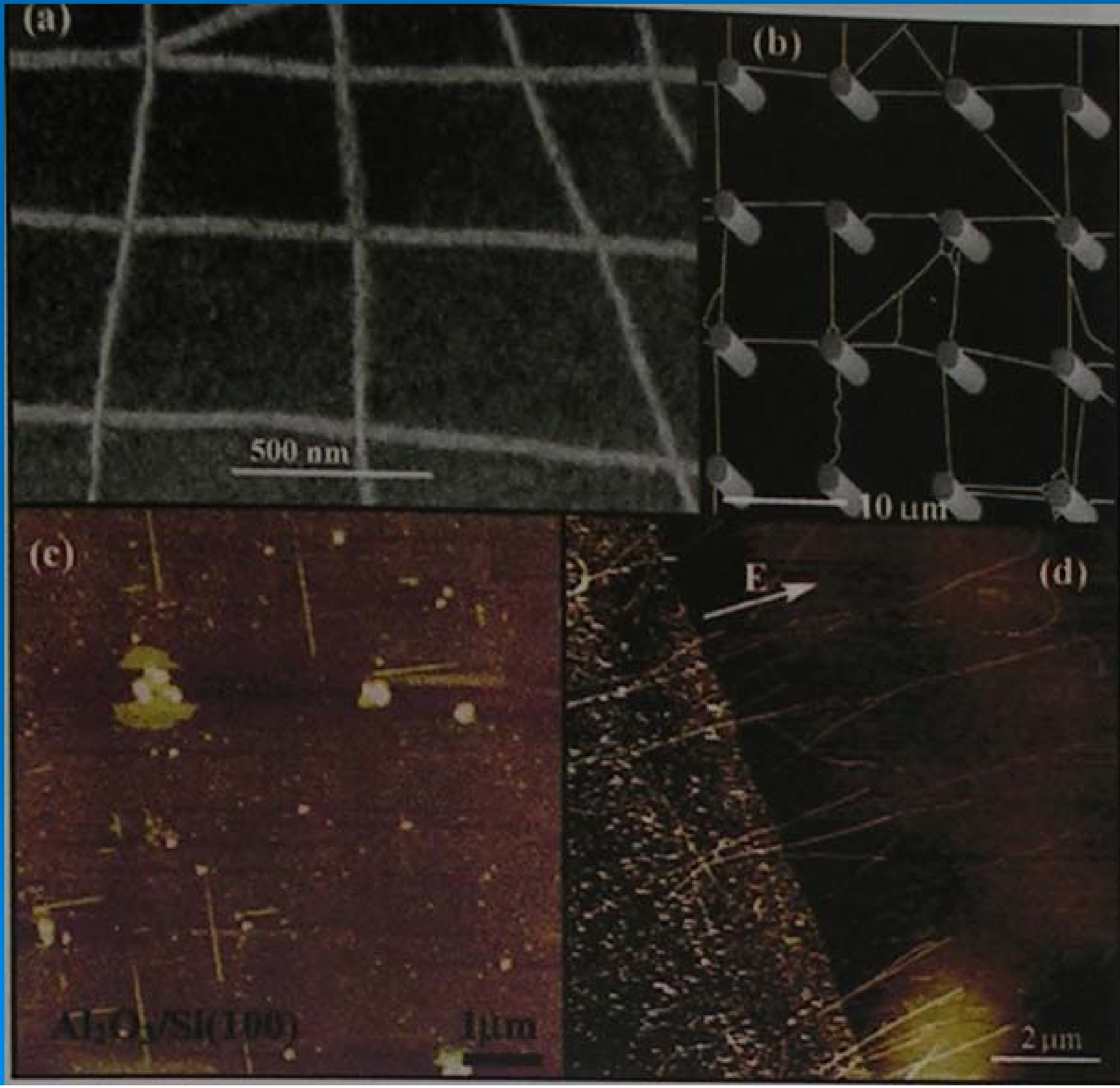


Processing and functionalization

- SWNTs are usually decorated with significant fraction of nanoscale impurities
- These as-made SWNTs must be purified through a process of reluxing the material in Nitric acid, then suspending the nanotubes in a basic solution and finally filtering
- Most critical issue in applicaton of nanotubes in nanoelectronics is the ability to assemble and integrate them in circuits

Assembly of nanotube arrays and nanocircuitry

- Controlled deposition from solution
  - SWNT arrays lying on a surface have been produced by selective deposition of nanolithographic templates
  - Extension of this method proved to be difficult due to the tendency of SWNTs to aggregate based on van der waals forces
  - Nice nanotube ropes can be fabricated with microfluidics combined with electric fields (fig 17a)


(a)
500 nm
(b)
10 um
(c)
$Al_2O_3/Si(100)$
1μm
E
(d)
2 μm

Assembly of nanotube arrays and nanocircuitry

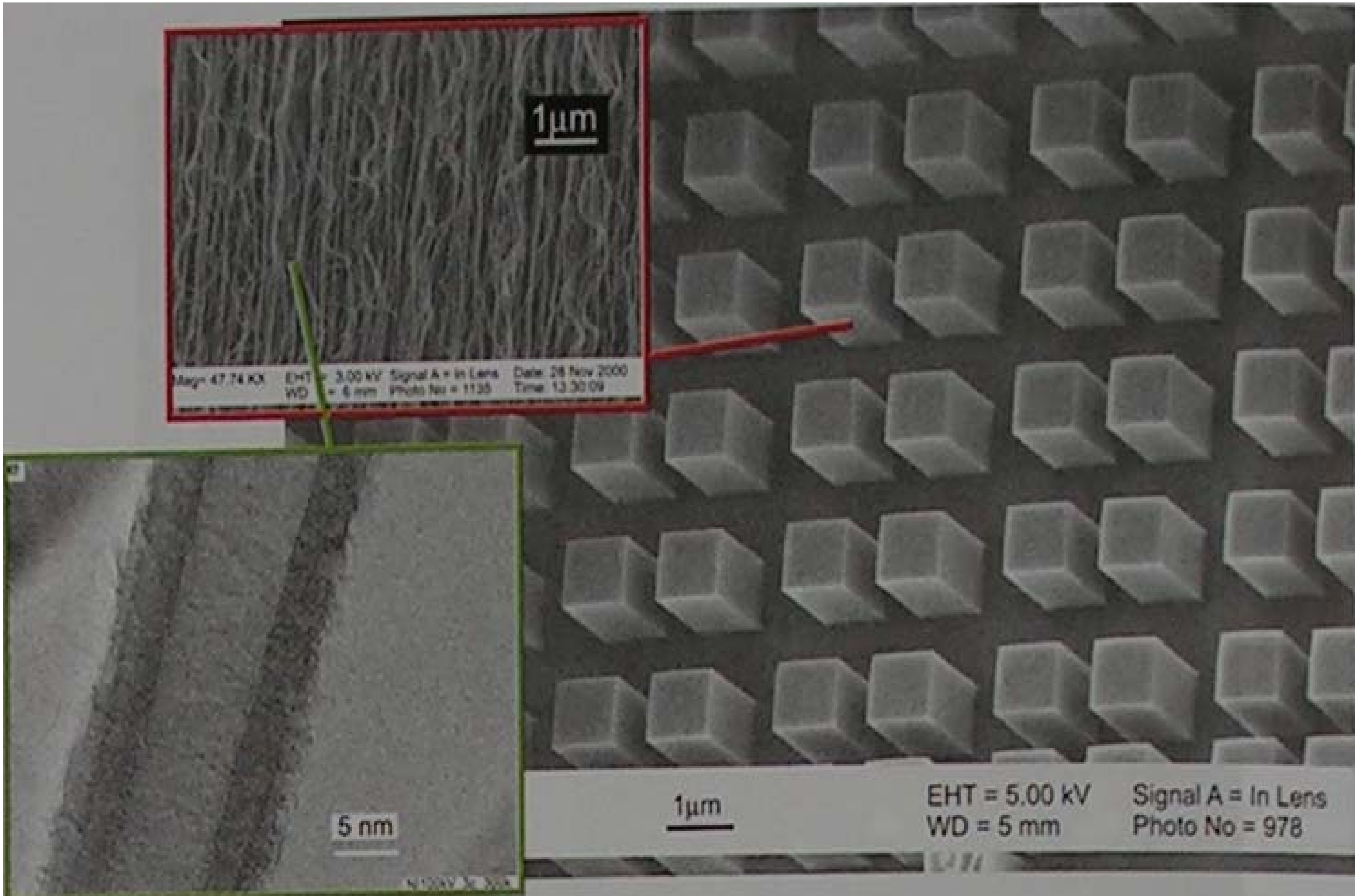
- Controlled growth of suspended networks
  - Controled growth by CVD is an attractive alternative to controlled deposition
  - Suspended networks of SWNTs can be grown(b)
- Lattice directed growth
  - Nanotubes prefer to grow parallel to lattice directions of the crystalline surface
- Vectorial growth
  - Application of electric field during growth of the tube (c,d)

Carbon Nanotube Interconnects

- Scaling the line widths increases resistance due to reduced cross section and increased scattering from the surface and grain boundaries
- If wires could be made without intrinsic defects and perfect surfaces, scattering could be avoided

Carbon Nanotube Interconnects

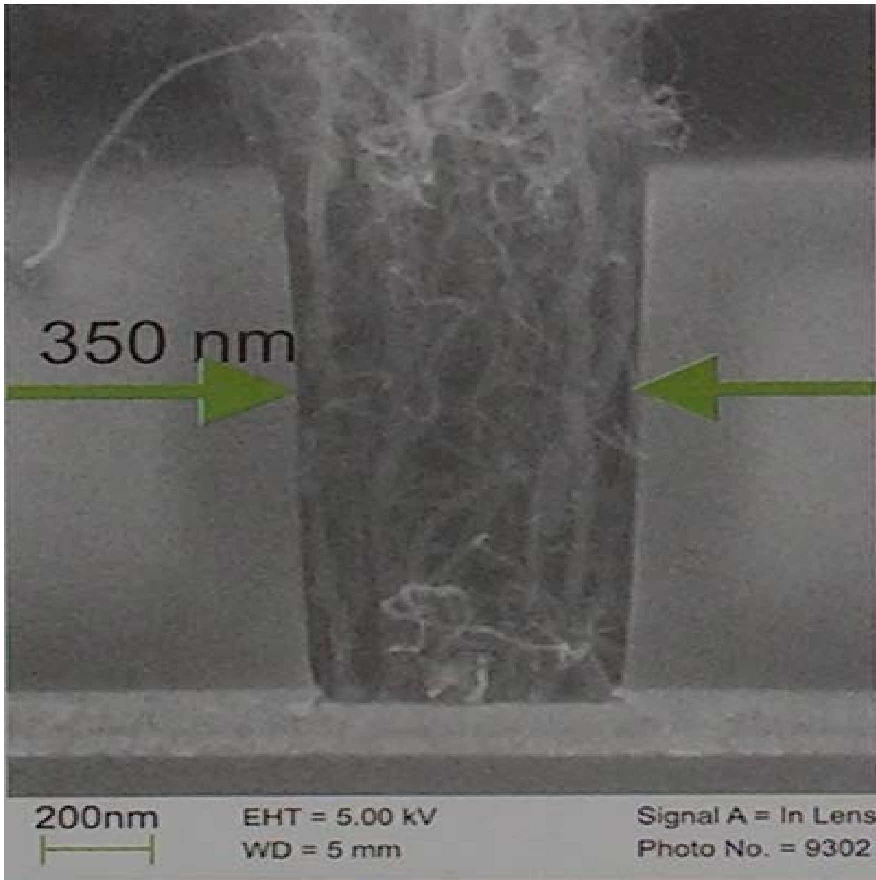
- Carbon nanotubes may fulfill this requirement
- Electron transport in tubes is ballistic within the electron-phonon scattering length
- Absence of scattering allows for much higher current densities than in metals
- Catalyst mediated CVD can be used to grow CNTs in predefined locations (fig 18)

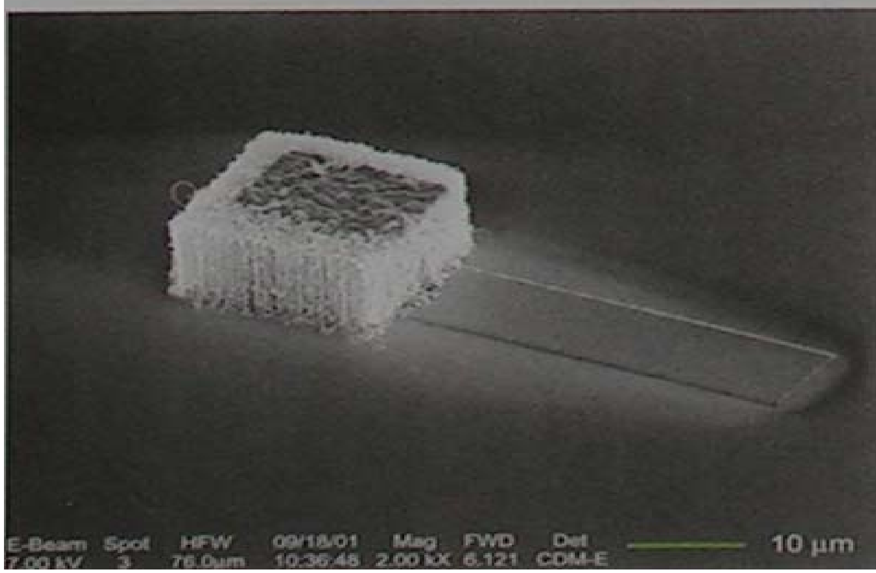


1µm
5 nm
1µm
EHT = 5.00 kV
WD = 5 mm
Signal A = In Lens
Photo No = 978

Carbon Nanotube Interconnects

- Nanotubes in vias
  - Vias are always prone to material deterioration such as void formation and breakdown because of high current densities
  - Nanotubes used in vias will be much less susceptible to damage due to high current densities
  - Figure (fig 19) shows a nanotube via and figure (fig 20) shows the ohmic I-V characteristic





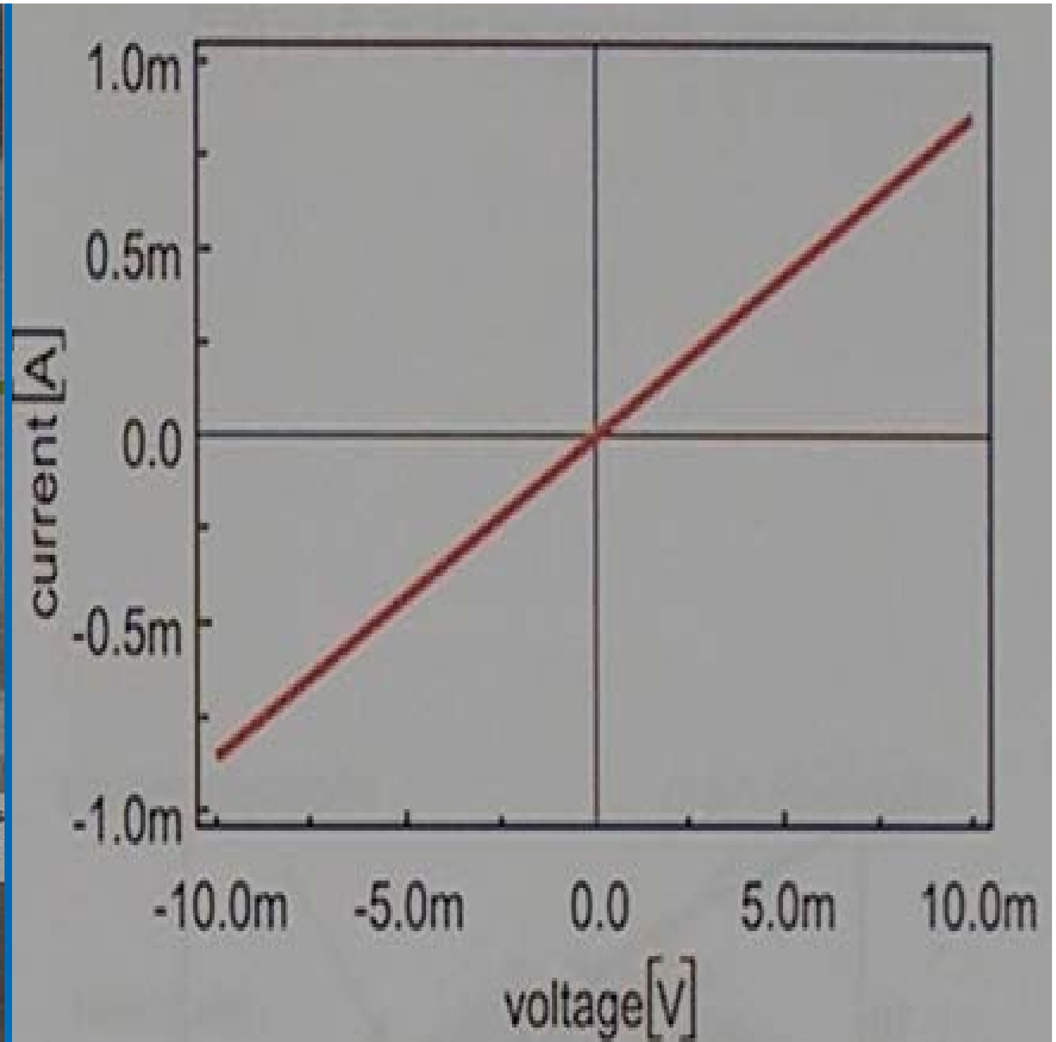


Figure 20: Current-voltage characteristic of a via filled with nanotubes. Ohmic behaviour is observed.

Carbon Nanotube Interconnects

- Maximum current density and reliability
  - Nanotubes exhibit a much higher current density than metals
  - MWNTs are investigated for maximum current as a function of time at elevated temperatures
  - Tubes carried densities of 5×10^9 A/cm^2 and 2×10^{10} A/cm^2 for more than 300 h. Copper fails at current densities of 10^7 A/cm^2

Carbon Nanotube Interconnects

- Signal propagation in nanotubes
  - Treatment of signal propagation in nanotubes is sophisticated
  - Propagation velocity of wave and signal rise time influenced by resistance, capacitance and inductance must be taken into account
  - Figure (fig 21) shows delay of copper and nanotube ohmic wires (neglected the inductance)

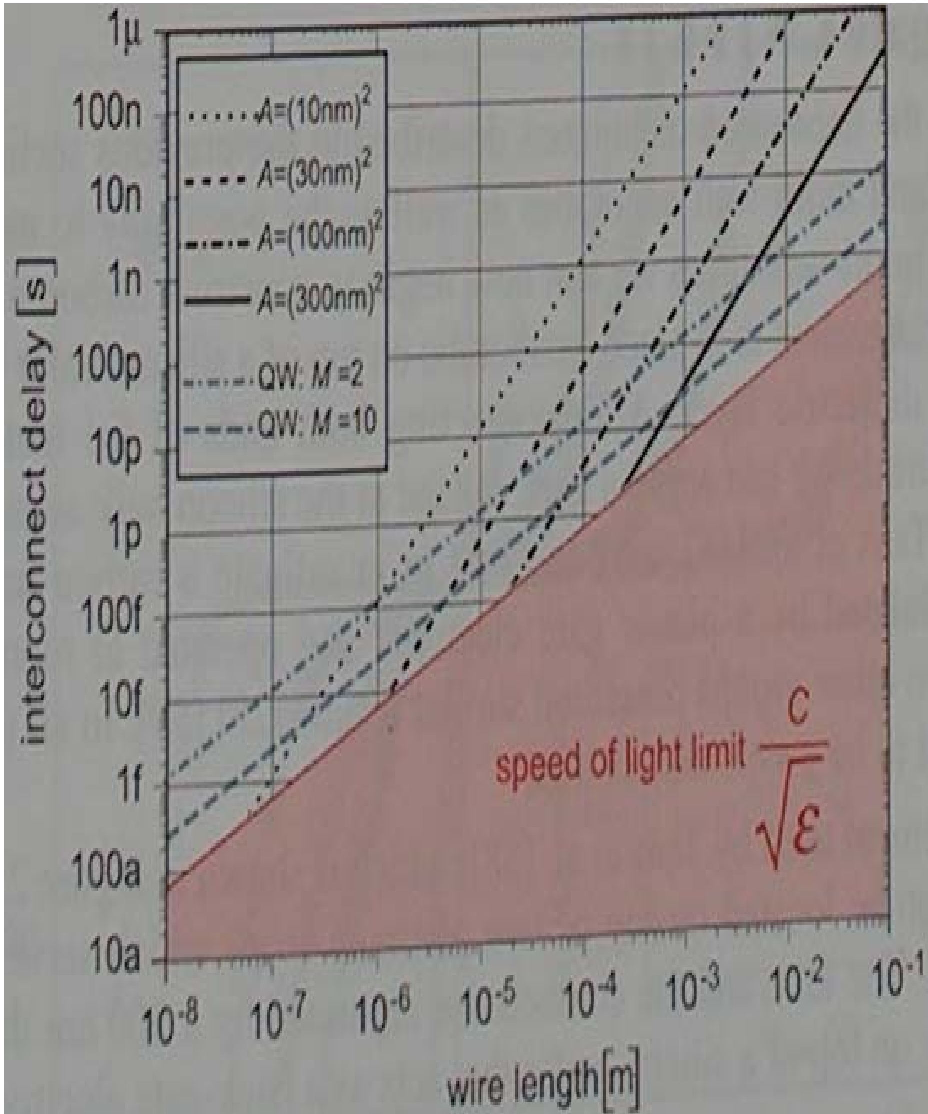


Figure 21: Signal delay in ohmic and ballistic wires as a function of wire length. The black lines represent the delays of ohmic wires with different cross sections A. Surface scattering has been taken into account. For wire lengths smaller than the intersections of black and red lines, the delay is governed by the speed of light and the relative permitivity of the dielectric. The nanotube wires display a completely different behavior to the ohmic wires, as shown by the blue lines. Due to the length-independent resistance, nanotubes exhibit better delay values for longer wires. *M* represents the number of conductive channels, that can be formed either by the number of occupied energy levels or by the number of shells of a multi-wall nanotube.

Carbon nanotube field effect transistors (CNTFETs)

- Comparison to MOSFET
  - In MOSFETs inversion channel can be considered as a 2-D conduction system
  - Unlike MOSFETs, the electron system of a nanotube is 1-D
  - The field applied by gate electrode can influence the conductivity of tube by accumulation or depletion of electrons (CNTFET)
  - Semiconucting SWNTs are best suited for CNTFETs

Carbon nanotube field effect transistors (CNTFETs)

- Tailoring of Nanotubes
  - Production of SWNTs is arduous and not compatible with parallel production required in IC technology
  - One step toward this is the use of MWNTs instead of SWNTs
  - Diameter and chirality of shells determines their energy gap and conduction type
  - It should be possible to choose the desired characteristics by contacting the appropriate shell

Carbon nanotube field effect transistors (CNTFETs)

- This was done by a group at IBM who managed to successively burn-off the outer shells of a MWNT located on contacts
- Figure (fig 22) shows this approach
- Figure (fig 23) shows the conductivity of tube as a function of back-gate voltage for 13 different shells that have been successively removed
- The energy gap widens as the tube diameter decreases

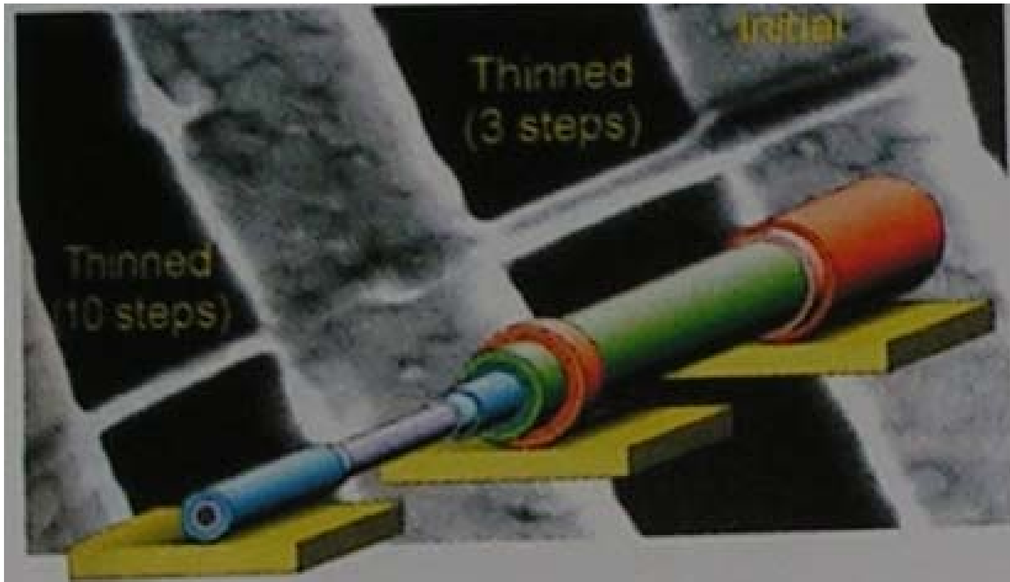


Figure 22: Controlled burn-off of the individual shells of a multi-wall nanotube between three adjacent contacts. In the first section three shells have been removed whereas ten shells have been stripped in the second section. The SEM picture and inset with schematic drawing are taken from [62].

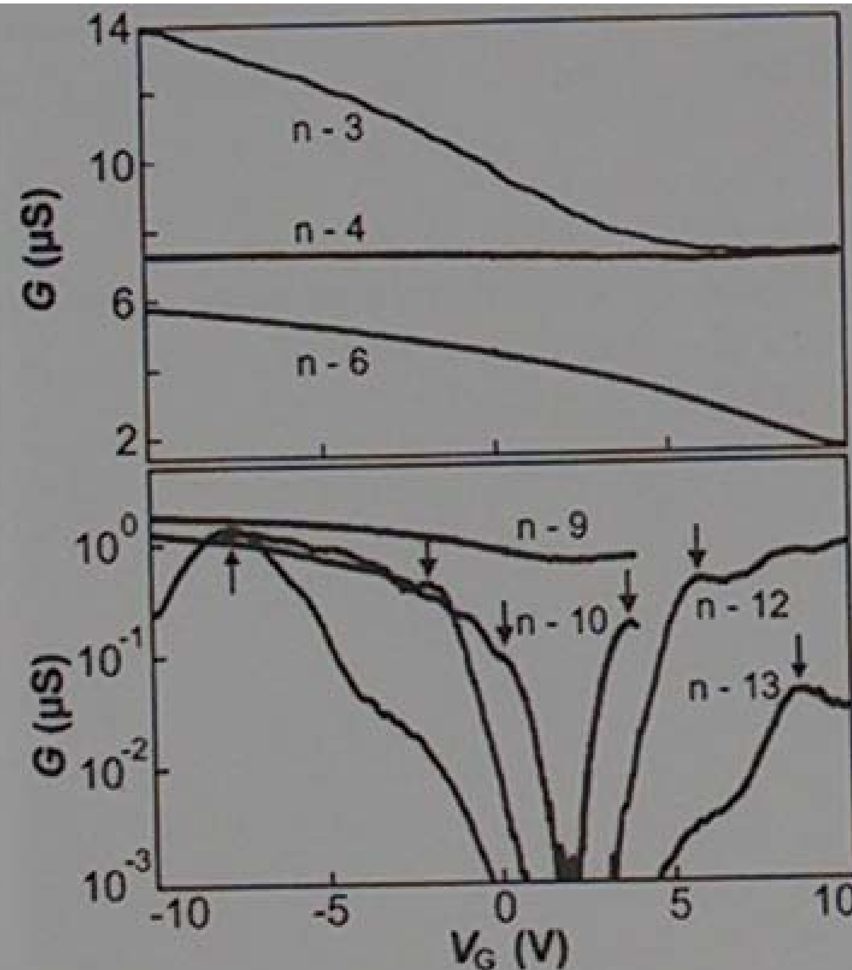
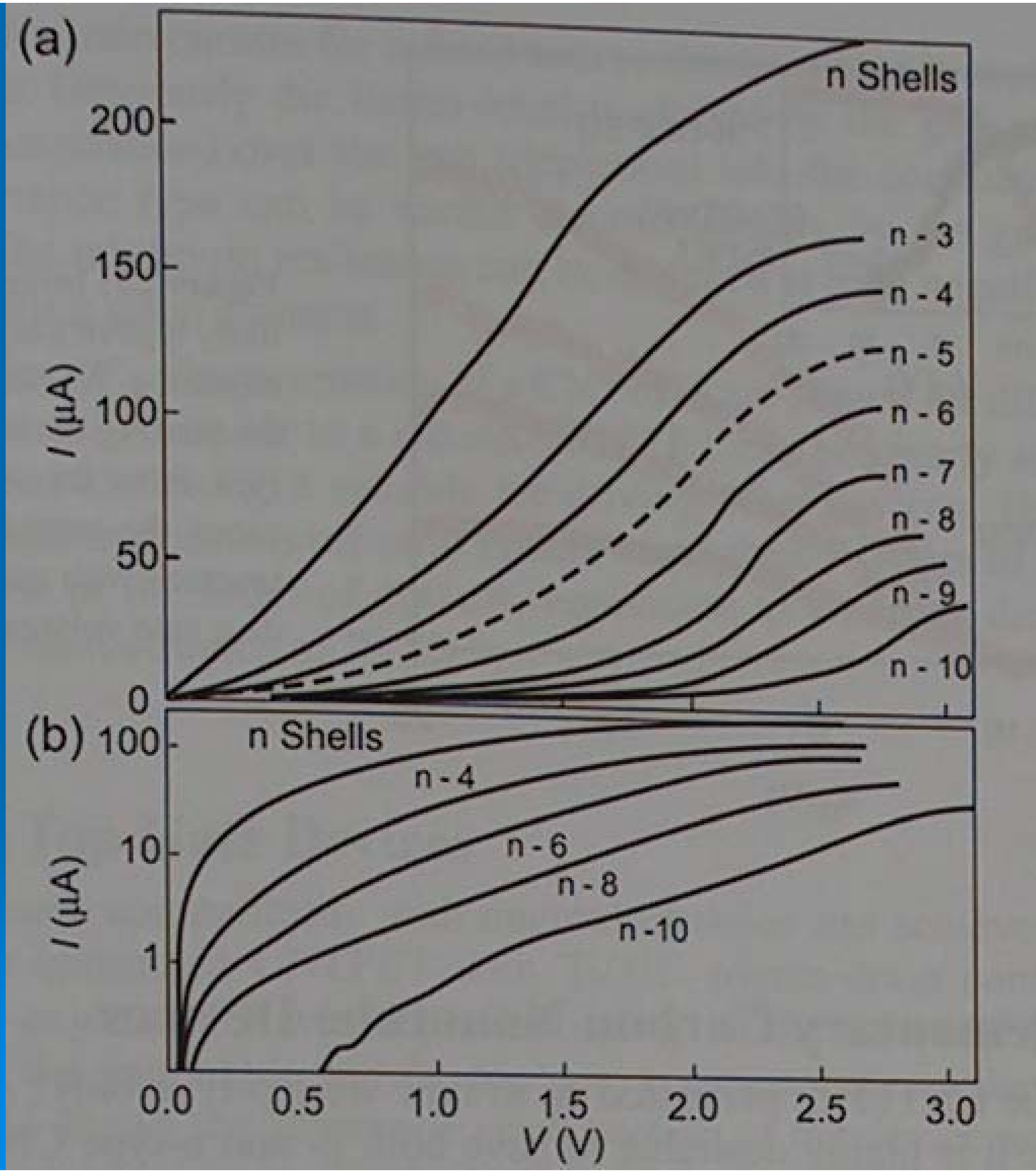


Figure 23: Conductivity of individual shells of a multi-wall nanotube (taken from [62]). The shells are removed by controlled current induced burn-off. The outermost shells show high conductivity with shell n-4 being metallic

Carbon nanotube field effect transistors (CNTFETs)

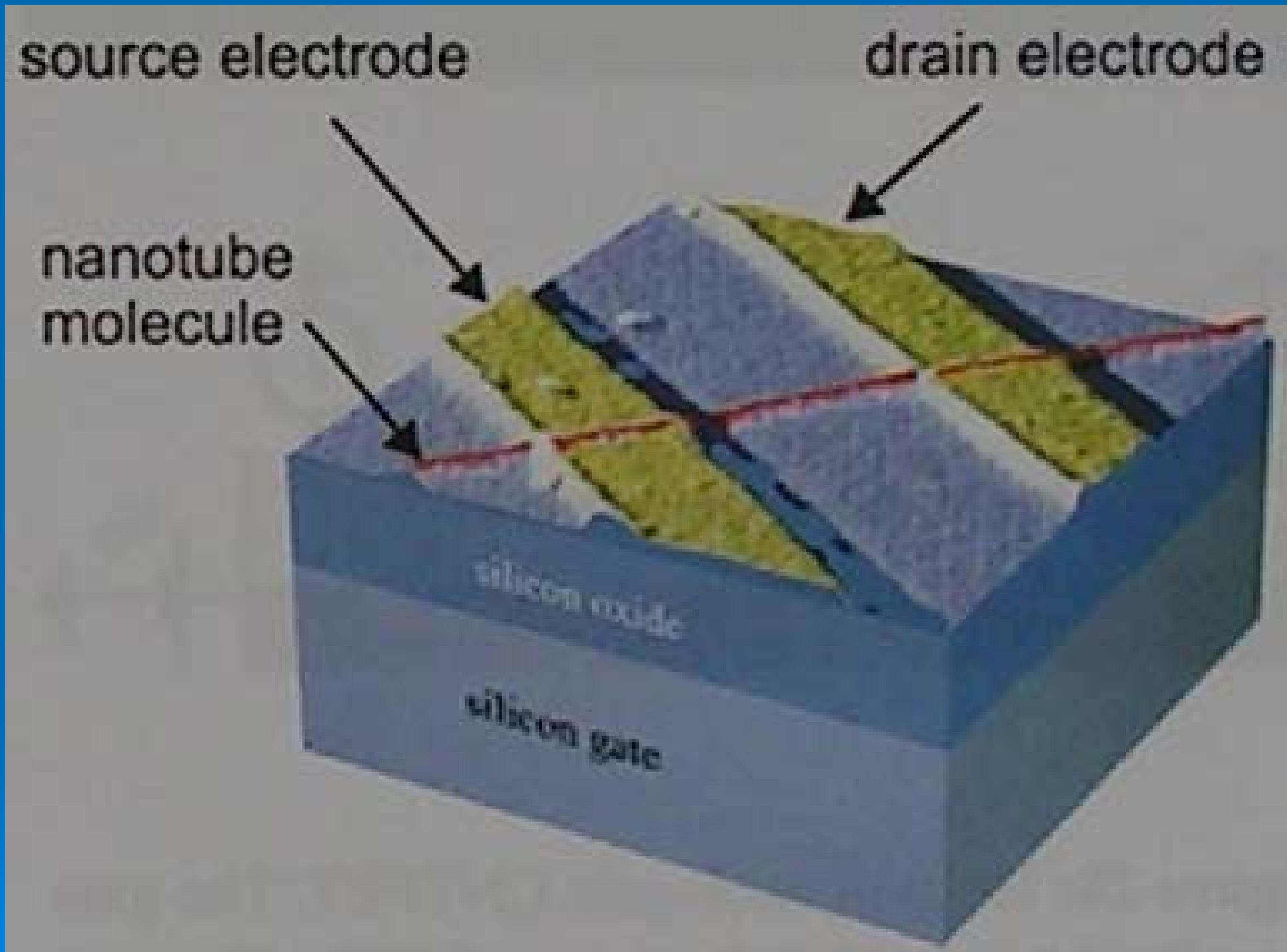
- Figure (fig 24) shows current-voltage characteristics for high source-drain voltages
- It is also shown that a bundle of SWNTs with arbitrarily mixed conductions can be separated from metallic species by applying a back-gate voltage to drive the semiconducting ones into depletion, while burning-off the metallic ones



(a)
n Shells
n - 3
n - 4
n - 5
n - 6
n - 7
n - 8
n - 9
n - 10
200
150
100
50
0
I (μA)
(b)
n Shells
n - 4
n - 6
n - 8
n -10
100
10
1
I (μA)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
V (V)

Carbon nanotube field effect transistors (CNTFETs)

- Back-gate CNTFETs
  - Simplest arrangement: place a nanotube on top of a silicon wafer covered with a SiO2 layer
  - After contacting both ends with an electrode, gate voltage is applied at silicon bulk acting as an overall gate electrode
  - This is shown in figure (fig 25)

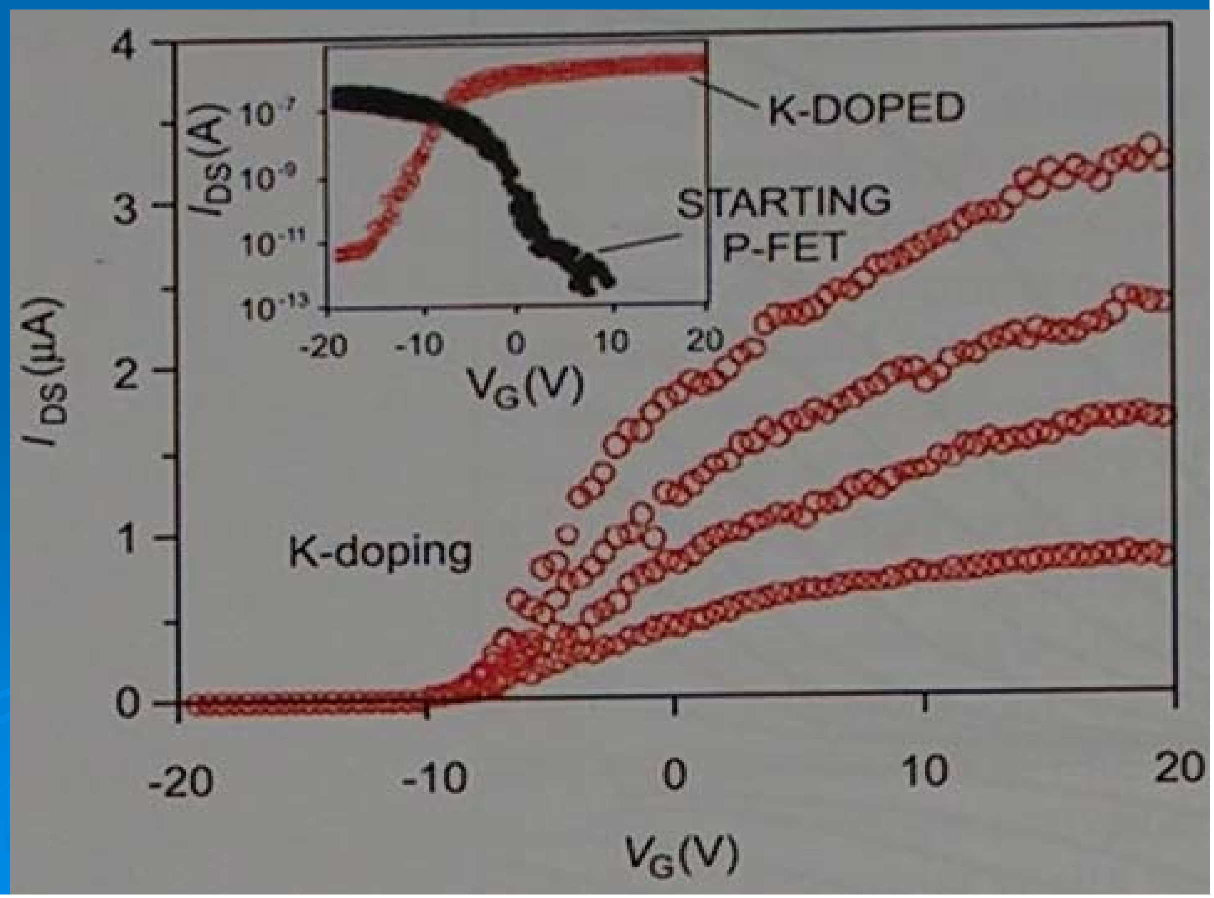

source electrode
drain electrode
nanotube
molecule
silicon oxide
silicon gate

Complimentary carbon nanotube devices

- As in MOSFETs, both p and n-type CNTFETs are required
- Fabrication of p-n junction within one nanotube has been achieved by covering one part of the tube with resist and exposing the other part to potassium vapor
- N-type behavior was also observed by applying potassium to nanotube ropes

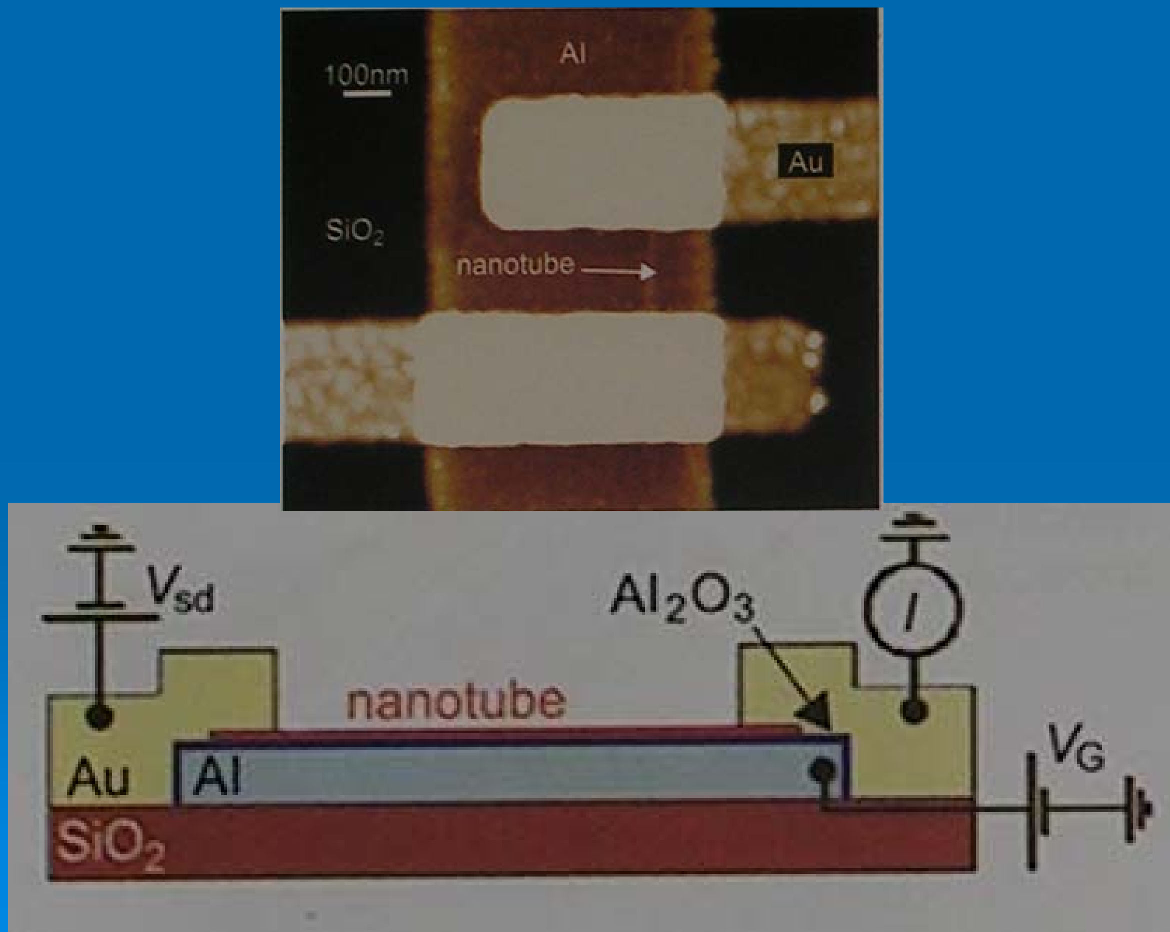
Complimentary carbon nanotube devices

- Figure (fig 27) shows the conversion of an originally p-type nanotube FET to n-type by k-doping and the resulting IDS vs. VG characteristics



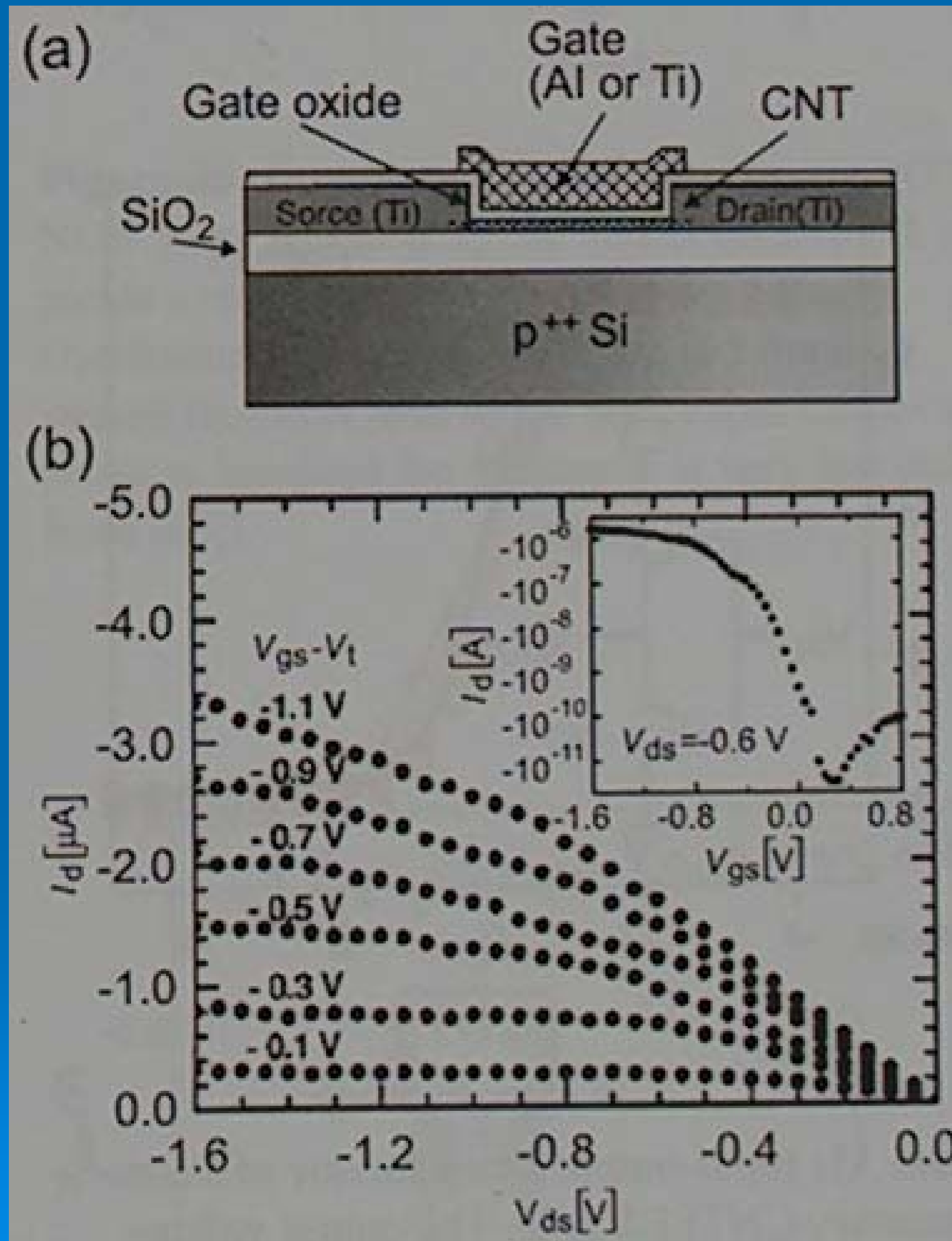
Isolated back gate devices

- Figure (fig 28) shows an isolated back-gate device implemented on thin Al2O3



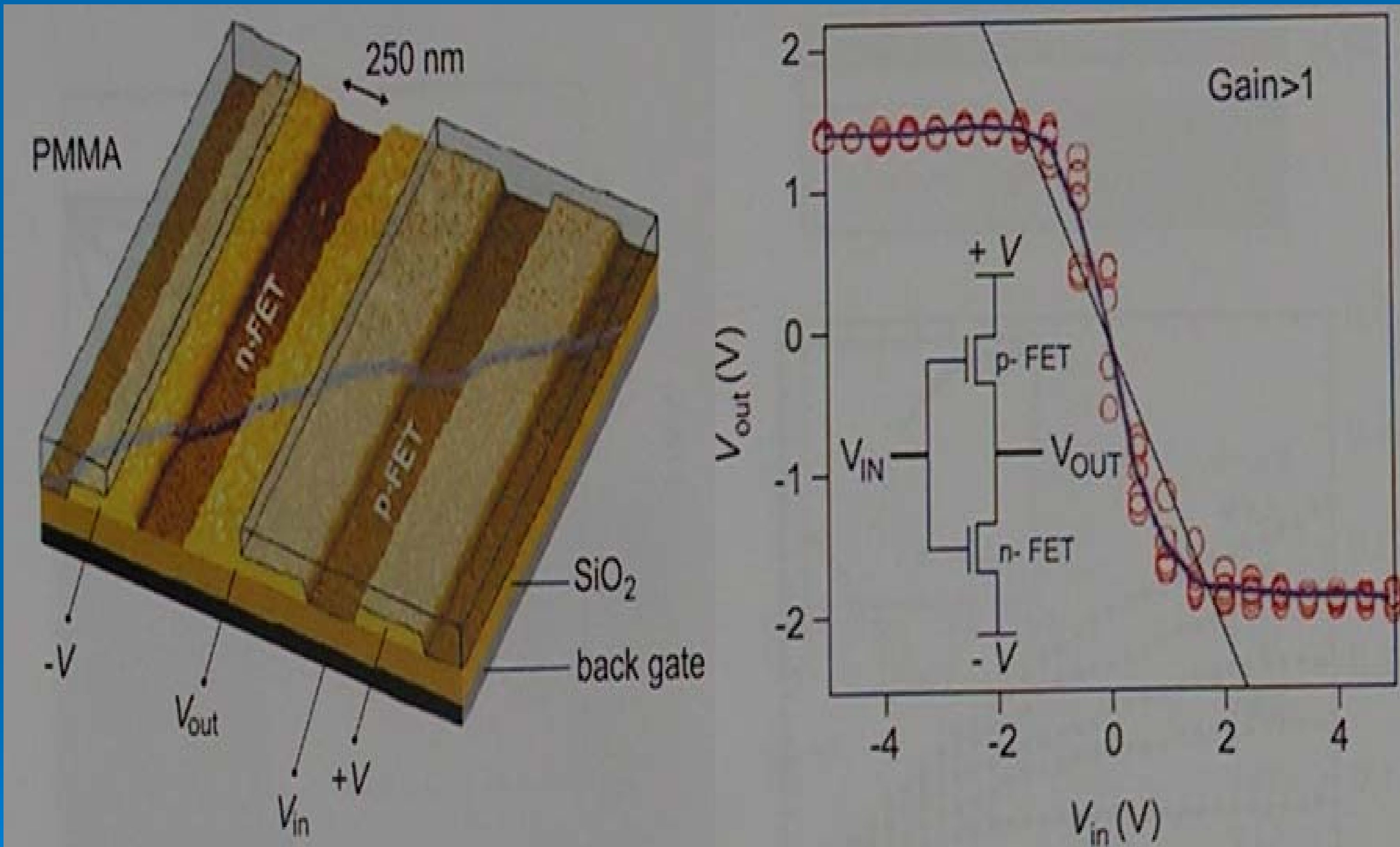
Isolated top gate devices

- An optimized CNTFET was presented with Ti/TiC source-drain contacts and a thin (15-20 nm) gate-oxide deposited on top of CNT (fig 31)
- Device can operate with gate swing of 1V
- N-type devices can be fabricated by annealing a p-type tube in inert atmosphere


(a)
Gate
(Al or Ti)
Gate oxide
CNT
SiO2
Sorce (Ti)
Drain(Ti)
p++ Si
(b)
Vgs-Vt
-1.1 V
-0.9 V
-0.7 V
-0.5 V
-0.3 V
-0.1 V
Id[μA]
Vds[V]
Vds=-0.6 V
Id[A]
Vgs[V]

Carbon nanotube circuits

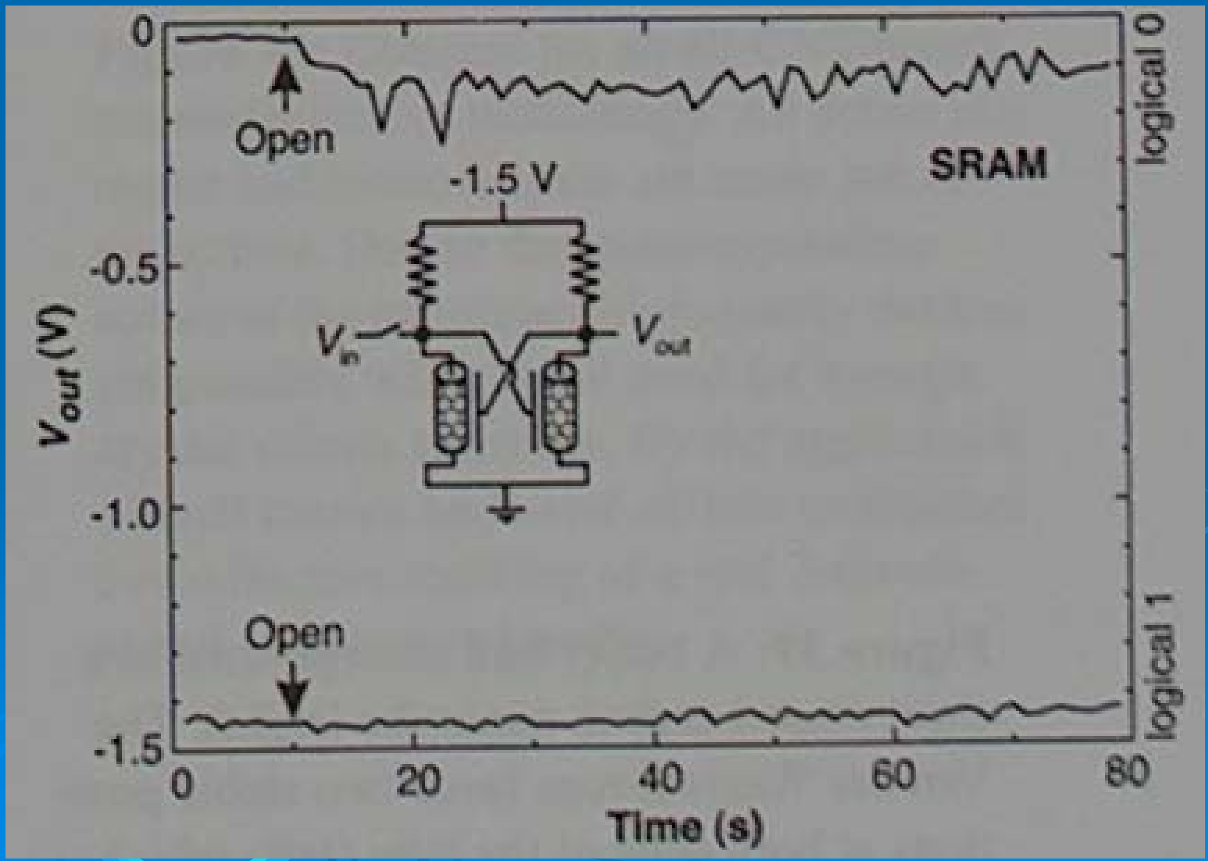
- Figure (fig 32) shows a mechanism for selectively doping part of a single nanotube placed on top of the contacts (n-type and p-tpye in series, controlled by a common gate)
- Figure (fig 33) shows the operation of the implemented inverter



250 nm
PMMA
n-FET
p-FET
SiO_2
back gate
-V
V_{out}
V_{in}
+V
Gain>1
+ V
p- FET
V_{IN}
V_{OUT}
n- FET
- V
V_{out} (V)
V_{in} (V)
2
1
0
-1
-2
-4
-2
0
2
4

Nanotubes for memory applications

- CNT-SRAMs
  - Figure (fig 36) demonstrates a SRAM unit cell implemented with CNTs



Nanotubes for memory applications

- Other memory concepts
  - Figure (fig 37) shows a crossbar array of nanotubes with one set separated from the other by a small distance provided by non-conducting supporting blocks

Nanotubes for memory applications

- The upper wires have two stable positions
  - One in their minimum elastic energy positions without contact to the lower cross-point wires
  - The other with the wires held in contact with lower wires, due to the van der waals force
  - In contact, electrical resistance reduces by orders of magnitude
  - The wires can be driven apart by charging them transiently with the same voltage
  - Thus a non-volatile memory is implemented