Chemical vapor deposition growth of carbon nanotubes: characterization and applications

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Structure of SWCNTs

Diameters: 0.6 - 2.0 nm

Length: 1 - 10^3 μm

Chiral Vector

\[ \mathbf{C} = n\hat{a}_1 + m\hat{a}_2 \]

Chiral Angle

\[ \theta = \tan^{-1}\left( \frac{2m}{n-3n} \right) \]

Diameter

\[ \frac{1}{\pi} \sqrt{n^2 + \left( \frac{1}{2} \right)^2 (m + n)^2} = \frac{C_h}{\pi} \]
Electronic structure of SWCNTs

Energy dispersion relations for 2D graphite

Wave vector $k$ for 1D CNTs in 2D Brillouin zone of graphite (hexagon) as bold lines for (a) metallic and (b) semiconducting CNTs

- CNT:
  - metallic: $n - m = 3q$
  - semiconducting: $n - m \neq 3q$

$q \in \mathbb{Z}$
Density of states of SWCNTs

Quantization of the wave vector along the circumferential direction leads to a density of states characterized by sharp van Hove singularities.

\[
D(E) = \frac{T}{2\pi N} \sum_{\pm} \sum_{\mu=1}^{N} \int \frac{1}{dE_{\mu}^{\pm}(k)} \delta(E_{\mu}^{\pm}(k) - E) \cdot dE
\]

1D density of states in units of states/C-atom/eV

(a) perfect (8,0) tube

(b) perfect (7,1) tube

semitconductor side

metal side
Structure of carbon nanotubes (CNTs)

Single-Wall Carbon Nanotubes (SWCNTs)

- Diameters: 0.6 - 2.0 nm
- Length: 1 - $10^3$ μm

Multi-Wall Carbon Nanotubes (MWCNTs)

- Diameters: 2.0 - 100 nm
- Length: 1 - $10^3$ μm

More complex is the behaviour for *multi-wall carbon nanotubes* (MWCNTs) because of interactions between adjacent layers.
Sample Preparation:
- Chemical Vapor Deposition (CVD)
- Substrates
- Catalyst film
- Growth

Characterizations:
- Scanning Electron Microscopy (SEM)
- X-ray Photoelectron Spectroscopy (XPS)
- Electron Energy Loss Spectroscopy (EELS)
- Raman Spectroscopy
- Transmission Electron Microscopy (TEM)

Applications:
- Nanolytography
- Nanomanipulation
- I-V measurements
- Gas Sensing
- Photoconductivity
- Field Emission
Sample Preparation:

- Catalyst particle in molten state absorbs carbon in vapor form (a) to form an alloy (b).
- As the particle becomes saturated with carbon, a solid CNT begins to extrude from the particle.
- The final location of the catalyst particle defines tip grown (c) or root grown (d) CNTs.

Stig Helveg et al. 
Sample Preparation:

Substrate:
Silicon, Glass, Aluminum, Copper, ...

Catalyst Film:
Ni or Fe

Clusterization of catalyst film:
Annealing in H₂ or NH₃

CNTs growth:
C₂H₂ : H₂
C₂H₂ : NH₃
Sample Preparation:

Vertical CVD

- Vertical CVD Pumping System
- Vertical CVD Vacuum Gauge
- Vertical CVD Heater Power Supply
- Vertical CVD HV Power Supply
- Vertical CVD Temperature Control

- Mass Flow 50 sccm
- Mass Flow 100 sccm
- Mass Flow 200 sccm

- C_2H_2
- H
- NH_3

Mass Flow

Temperature Control

Heater Power Supply

HV Power Supply

V_1

V_2

V_3

V_4

V_5

V_6
Sample Preparation:

- CVD process

[Diagram showing temperature profile and sample position]
Synthesis of CNTs: Chemical Vapour Deposition (CVD)

New CVD reactor
Characterizations:

\[ T = 500 \, ^\circ C \]

\[ T = 700 \, ^\circ C \]
Characterizations:
TEM: Morphology
CNT growth at 500 °C

**Characterizations:**

- Elongated structures ($l \sim 50 – 150$ nm, $d \sim 30 – 50$ nm)
- The structure is more similar to a filled cylinder than to a tube
- At the edges round particles are visible with diameter $5 – 20$ nm.
Characterizations:

TEM: Chemical Composition
CNT growth at 500 °C

Unfiltered
Energy filter **Carbon** edge
Energy filter **Nickel** edge

The particles \((d \sim 20 \text{ nm})\) are made of Nickel and are located close to the apex of the structures.
The external shells are not well graphitized.

Characterizations:

TEM: Crystalline Structure
CNT growth at 500 °C

Around the grains there is a crystalline core.
• Tubes with hollow interior ($l \sim$ micron scale, $d_{\text{ext}} \sim 10 – 30$ nm).

• Several tubes look bended

• At the edges particles are visible with diameter 5 – 20 nm.

• Inclusions of particles are also present along the tubes.
Characterizations:

TEM: Chemical Composition
CNT growth at 700 °C

Unfiltered

Energy filter **Carbon** edge

Energy filter **Nickel** edge
TEM: Chemical Composition
CNT growth at 700 °C

Characterizations:

Unfiltered

Energy filter Nickel edge

Long Nickel inclusions (defects) are observed
Characterizations:

TEM: Crystalline Structure
CNT growth at 700 °C

- Outer diameter: 15 – 25 nm
- Inner diameter: 5 – 10 nm
- Average # of tubes: 10 – 15
TEM: Tubes Capping
CNT growth at 700 °C

Characterizations:

- Bended tubes (6)
- Crystalline tubes (8)
- 6.8 nm
- 10.9 nm

- Crystalline tubes (14)

- Capped tubes
- Crystalline tubes (9)
- 6.9 nm
- 6.1 nm
- Polycrystalline shell

- 5 nm
In proximity of the catalyst the carbon is highly graphitized.

Uncapped Tubes: cores

TEM: Particle Inclusion
CNT growth at 700 °C
Self-patterned Growth: Black & White

Applications:
Nanolithography &
design for the CNTs growth

Applications:

GINT collaboration
Applications:

lift-off of Nichel film (3 nm)

Electron beam exposure

GDSII mask design

After developing

Nichel film deposition

Aceton bath
Applications:

GDSII mask design
Applications:
Applications:
Applications:
Selective Chemical Vapour Deposition growth of carbon nanotubes on submicrometric Ni patterns fabricated with Scanning Probe Nanolithography

Digital Instruments D5000 Microscope (Nanoscope IV controller) using commercial silicon tips (frequency range 310-370 kHz) scanned by means of a Veeco Nanoman closed loop XY head.
(a) 18.0 μm × 2.5 μm AFM micrograph of 13 nm PMMA on SiO2 substrate after nanoindentation.
(b) AFM micrograph of the same area of panel (a) after deposition of 3 nm of Ni and subsequent lift-off of resist.
(c) Height profile of the written line on PMMA (see panel (a)).
(d) Height profile of a Ni stripe, evidenced in panel (b).

(a-c) 5 μm × 3 μm AFM and SEM (60000x) micrographs of three Ni stripes before (a-b) and after (c) growth of CNTs.

Applications:

Manipulation and electrical characterization of carbon nanotubes by using nanomanipulators inside SEM
CNT metal contact

Applications:

CNT on surface/metallic pads:

- CNT structural distortions...
- ... influence on the CNT intrinsic electronic transport properties

Schematic picture of CNT distortion across metallic pads

It is therefore advantageous to perform electrical measurement on CNTs in the **free space**, and it is also desirable to have the possibility to manipulate a characterized carbon nanotubes into predetermined position for device construction.

CNT 3D manipulation in free space (!)
Applications:

**CNT 3D manipulation in free space**

- no structural distortions
- no post-processing process (lift off, metallization, etc...)

Nanomanipulation under Scanning Electron Microscopy:

![Diagram showing nanomanipulator and SEM](image)

CNT manipulation@NIST
Applications:

- Viewing and placement of probe contacts at specified locations along a CNT.
- Three dimensional freedom=all the aspects of the investigated CNT can be explored.
- No ambiguities related to the interpretation of the results of electrical and mechanical experiments.
Applications:

- MWCNT manipulations under SEM
- MWCNT as grown on Ni wire by CVD
- I-V characterization of MWCNT
- I-V characterization of CNT/CNT junction

“Nanowelding” via Electron Beam Induced Deposition
Applications:

- MM3A-nanoprobe system (Kleindeik Company)
- Scanning Electron Microscopy (ZEISS, LEO 1430)
- The manipulators are coupled with a Keithley-236 electrometer to perform electrical current-voltage (I-V) measurements.

Schematic of the I-V apparatus

Approaching CNT...
MWCNT grown on Ni template:
low contact barrier at the Ni/CNT interface

... The effect of the Electron Beam irradiation in improving the W/CNT contact has been investigated ...
I-V vs Electron Irradiation

1) Approaching CNT protruding from the Ni tip
2) I-V acquisition
3) Electron beam irradiation of the contact area (10 keV, 10 min)
4) I-V acquisition after each irradiation cycle

Applications:
Applications:
Applications:
Applications:

I-V Curve Vs. Time Exposure to e⁻ Beam

Current (µA)

0.000

0.002

0.004

0.006

0 min Beam Exposure

Voltage (V)

0.0

0.5

1.0

1.5

2.0

Voltage (V)

0.0

0.5

1.0

1.5

2.0

CNT W Tip

Contact resistance

CNT W Tip
I-V vs Electron Irradiation: RESULTS

Non linear (linear) dependence of the current in the high voltage (low voltage) range observed is perfectly consistent with the presence of a tunnel barrier in correspondence of the metallic CNT/movable junction

- Resistance at W/CNT junction:
  - Contact area
  - nature of metal electrode
  - CNT/metal distance
Electron beam Induced deposition

CNT e⁻ beam damaging ?

- Exposing medium region of a suspended CNT...
- I-V before \((a)\) and after \((b)\) the exposure...
- No variations observed \((c)\).

No damaging effect on the CNT structure (10 keV, 1 hour exposure)

Applications:
Applications:

Welding of CNTs

- \( R_{\text{sat}} = 120 \, \text{k}\Omega > 12.9 \, \text{k}\Omega \)

- After the welding, single nanotube can be pulled out from the Ni surface ...

- ... contacting another CNT ...

- a stable CNT/CNT ohmic junction can be produced by EB nanowelding.

Applications:

**CNT welded on AFM tip**
I-V measure on CNTs
Micromanipulator Kleindiek
Applications:

Photoconductivity in defective carbon nanotubes sheets under UV-Vis-NIR radiation

Applications:

**Photoconductivity**

Photocurrent \( I_{ph} = I_{light} - I_{dark} \)

Relatively large area samples show, under white light illumination, a wide-range linear behavior of the photocurrent as a function of bias voltage and optical power density.
The spectral photoresponse has been determined in terms of the photoconductance ($G$) normalized to the incident photon flux, $n_{ph} = \lambda F / hc$, as given by:

$$G = \frac{I_{ph}}{(SV_{pol} n_{ph})}$$

where $c$ is the speed of light, $h$ is the Planck constant, and $S$ is the illuminated area.

The spectral photoresponse of all the samples increases with increasing photon energy and is strongly correlated to the absorbance.
Applications:

Field emission from a selected multiwall carbon nanotube

We have shown that the emission phenomenon is very well described by a series resistance modified Fowler–Nordheim model.

M. Passacantando et al., Nanotechnology 19 (2008) 395701
M. Passacantando et al., Carbon 45 (2007) 2957
Applications:

This is an original method to limit or suppress the field emission current from a single nanotube through the controlled and selective deposition of carbonaceous species on its apical region.

This result opens several perspectives for the study of the field emission properties of carbon nanotube arrays, enabling the switching of selected single emitters, as well as for technological applications in which tunable nanosized emitters might be needed.

Passacantando et al. Nanotechnology 19 (2008) 395701
Low ($T=400 \, ^\circ C$) temperature Growth

CNT / Glass
CNT / Copper
**Structural analysis: Raman Spectroscopy**

- **RBM**: radial breathing mode $\sim 230 \text{ cm}^{-1}$
- **G-band**: crystallographic graphitic order $\sim 1582 \text{ cm}^{-1}$
- **D-band**: structural defects $\sim 1350 \text{ cm}^{-1}$

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![Graphene Raman Spectroscopy](image)

- $\lambda = 633 \text{ nm}$
- **D**: 750°C
- **G**: 750°C

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**Catania, 6th October 2010**
Structural analysis: Raman Spectroscopy

RBM

\[ \lambda = 633 \text{ nm} \]

\( 277 \text{ cm}^{-1} \)

\( 258 \text{ cm}^{-1} \)

\( 247 \text{ cm}^{-1} \)

\( 190 \text{ cm}^{-1} \)

\( 300 \text{ cm}^{-1} \)

\( \text{Si-c} \)

Catania, 6th October 2010
Synthesis of graphene: Chemical Vapour Deposition (CVD)
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Thanks!
Photosensor made of MWCNTs: details of device fabrication

The device

Pt electrodes

MWCNT film

Au strips

Multipin sample holder

Rome, 17th September 2010
Photoelectric measurements

The sample holder has been connected to external circuit for electrical measurements (Keithley-236 electrometer controlled by LabView software).

Standard optical fiber: light spot of ~0.8 mm²

Support for external electrical contact and horizontal movement (step 0.625 mm)

Rome, 17th September 2010
Photoconductivity of MWCNT by white light

Contacts: Ohmic – Schottky

$I_D$: dark current
$I_L$: current generated by a white light by a LED

Pt
Si$_3$N$_4$
Si (100) n-type
Si$_3$N$_4$

Rome, 17th September 2010
The photoconductivity measurements show that only the more defective MWCNTs grown at 500 °C have a noticeable photosensitivity.
Rome, 17th September 2010

Photoconductivity of MWCNT by LED light

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>380</th>
<th>395</th>
<th>470</th>
<th>518</th>
<th>590</th>
<th>640</th>
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</thead>
</table>

LED light

![Graph showing photoconductivity of MWCNT by LED light with voltage (V) on the x-axis and current (µA) on the y-axis.](graph.png)

- Dark current
- 640 nm
- 590 nm
- 518 nm
- 470 nm
- 395 nm
- 380 nm
$I_{Ph} = I_L - I_D$

The $I_{Ph}$ has been normalized to the incident photon flux ($n_{ph}$):

$$n_{ph} = \frac{\lambda F}{hc}$$

where:

- $\lambda$ = wavelength of radiation [m]
- $F$ = power density [W/cm$^2$]
- $h$ = Planck constant [$6.626068 \times 10^{-34}$ J·s]
- $c$ = speed of light [299 792 458 m/s]
- $S$ = illuminated area [cm$^2$]
The spectral photoresponse has been determined in terms of the \textit{photoconductance} \((G)\) normalized to the incident photon flux:

\[
G = \frac{I_{ph}}{SV_{pol} n_{ph}}
\]

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<th>Wavelength (nm)</th>
<th>Range plateau (V)</th>
<th>G average (s(\Omega)^{-1})</th>
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<td>380</td>
<td>-15 (\rightarrow) -7,5</td>
<td>(1,0183 \times 10^{-21})</td>
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<td>(1,62742 \times 10^{-21})</td>
</tr>
<tr>
<td>590</td>
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<td>(2,34097 \times 10^{-21})</td>
</tr>
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<td>(3,16456 \times 10^{-21})</td>
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Photoconductance of MWCNT by LED light

\[ G = \frac{I_{ph}}{SV_{pol} n_{ph}} \]
Application: Photosensor made of MWCNTs

- Standard optical fiber: light spot of ~0.8 mm²
- Support for external electrical contact and horizontal movement (step 0.625 mm)
- Cross view of the device
- Temperatures: $T = 500 \, ^\circ C$ and $T = 750 \, ^\circ C$

Catania, 6th October 2010
Application: Photosensor made of MWCNTs

$I_D$: dark current

$I_L$: current generated by a white light by a LED

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Graphs showing the current-voltage characteristics for different conditions and wavelengths.
Applications:

Growth over a Pt/Si$_3$N$_4$ Gas sensor device

Pt electrodes 50 nm+10 nm Ta

30 μm

Si$_3$N$_4$

Si$_3$N$_4$

Back Heater

Applications:

Growth over a Pt/Si$_3$N$_4$ Gas sensor device

Pt electrodes 50 nm+10 nm Ta

30 μm

Si$_3$N$_4$

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