# UNIVERSITA' DEGLI STUDI DI SALERNO

FACOLTA' DI SCIENZE MATEMATICHE, FISICHE E NATURALI


TESI DI LAUREA IN FISICA

# *PROPRIETÀ FISICHE ED APPLICAZIONI DEI NANOTUBI DI CARBONIO*

**Relatore: Dott. A. Di Bartolomeo**

**Correlatore: Dott.ssa A. Nigro**

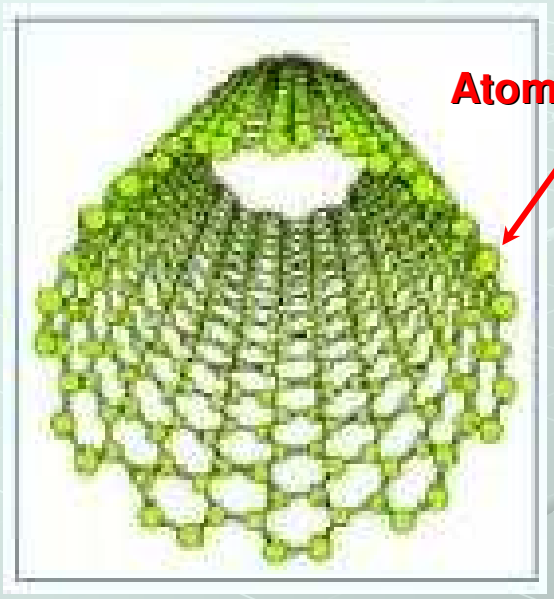
**Candidato: Davide Mancusi**

# RICERCA E SVILUPPO DI MATERIALI E PROCESSI NANOTECNOLOGICI

- **Nanotecnologie**: complesso di tecniche e discipline scientifiche atte a studiare, progettare, fabbricare e caratterizzare dispositivi con dimensioni inferiori al micrometro.

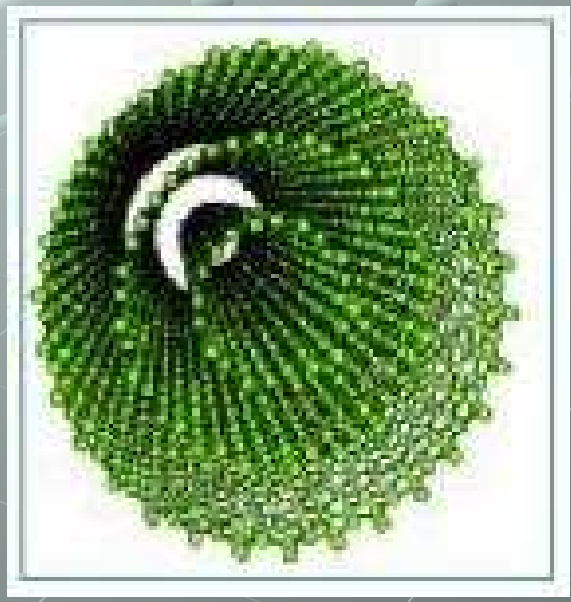
- **Applicazioni**: realizzazione di dispositivi elettronici, ottici, meccanici ed elettromeccanici per le applicazioni tecnologiche e nel campo della medicina.

# NANOTUBI DI CARBONIO




Nanotubo di carbonio a parete singola
(Single – Walled Carbon NanoTube)

Nanotubi di carbonio a parete multip
(Multi – Walled Carbon NanoTube)



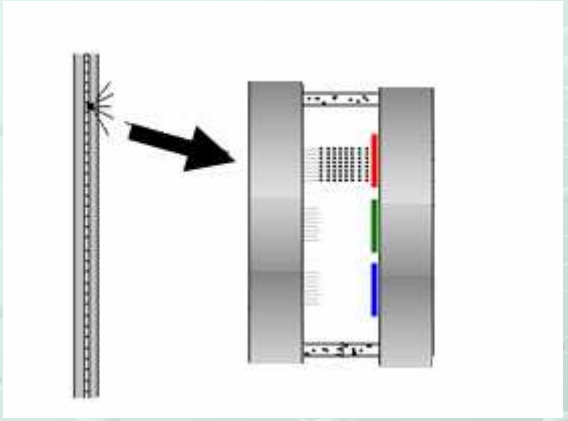
# NANOTUBI DI CARBONIO

| PROPRIETA' | CNT | CONFRONTO |
|---|---|---|
| Dimensioni | 0.6 – 2 nm (SWNT)<br>0.6 – 100 nm (MWNT) | Conduttori di Si:<br>almeno 50 nm |
| Conduttività elettrica | Semiconduttori o metalli<br>$10^9$ A/cm$^2$ | Conduttore di Rame<br>$10^6$ A/cm$^2$ |
| Emissione di campo | 1-3 KV/μm da singolo CNT | Punta di Molibdeno<br>50 – 100 KV/μm |
| Conduttività termica | 6000 W/m·K | Diamante<br>3320 W/m·K |
| Densità | 1.4 g/cm$^3$ | Alluminio:<br>2.7 g/cm$^3$ |
| Resistenza a trazione | ~ 75 GPa (SWNT)<br>~ 150 GPa (MWNT) | Acciaio : 2 GPa<br>con densità da 3 a 6 volte maggiore |
| Modo di elasticità | 1054 GPa (SWNT)<br>1200 GPa (MWNT) | Acciaio : 208 GPa |
| Costi | 1500 $/g | Oro<br>10 $/g |

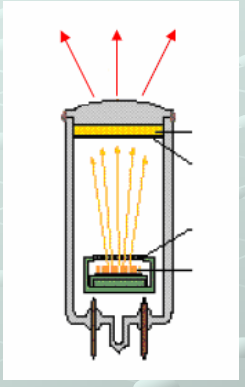
# NANOTUBI DI CARBONIO

- Struttura e proprietà elettroniche
- Processi di fabbricazione
- Applicazioni
- Risultati sperimentali
  - R(T) su film di MWNT
  - Conduttività di materiali compositi (PE/MWNT)
  - Emissione di campo da MWNT allineati

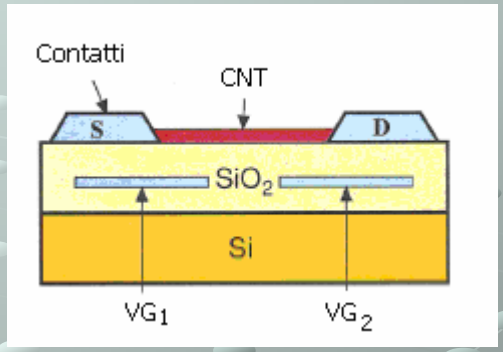
# APPLICAZIONI DEI CNT



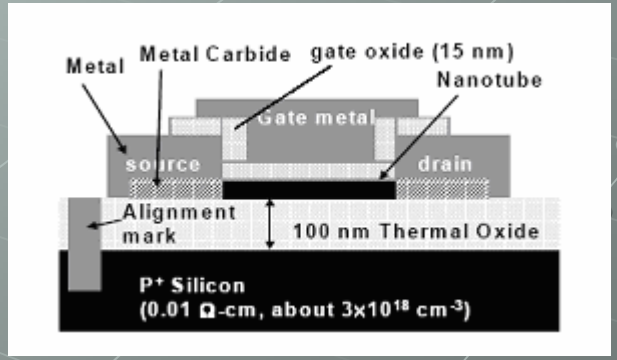
Display a emissione da CNT



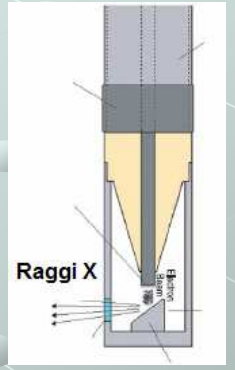
Lampade a CNT




Diodi




CNT FET

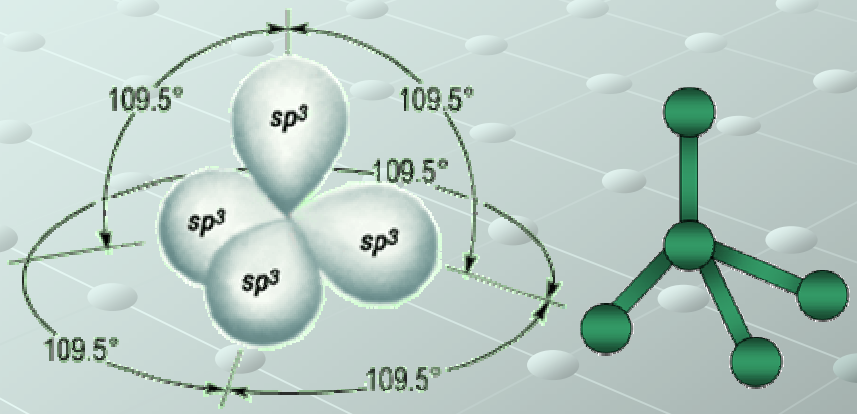




Tubo a RX miniaturizzato

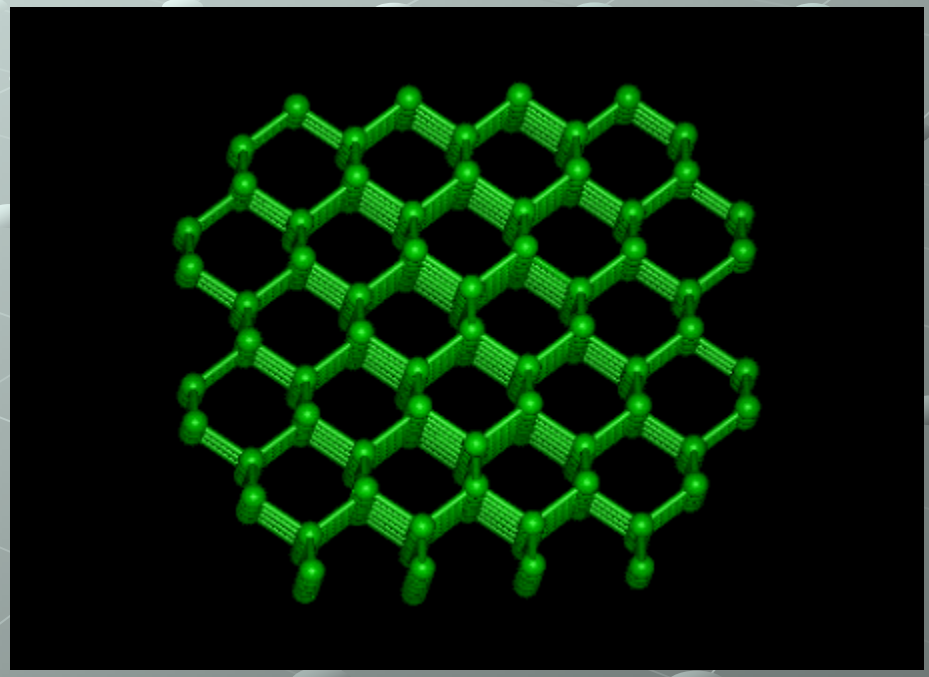
# STRUTTURA E PROPRIETÀ DEI CNT

## FORME ALLOTROPICHE DEL CARBONIO (Z=6)
### (CONFIGURAZIONE ELETTRONICA ESTERNA $2s^2\ 2p^2$)



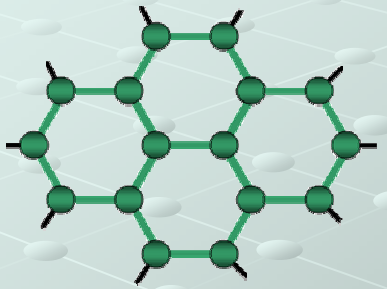

**Orbitale ibrido $sp^3$**

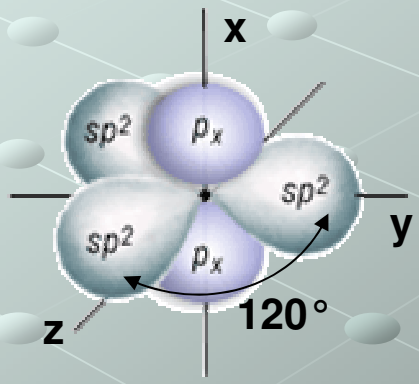
**DIAMANTE**



# STRUTTURA E PROPRIETÀ DEI CNT

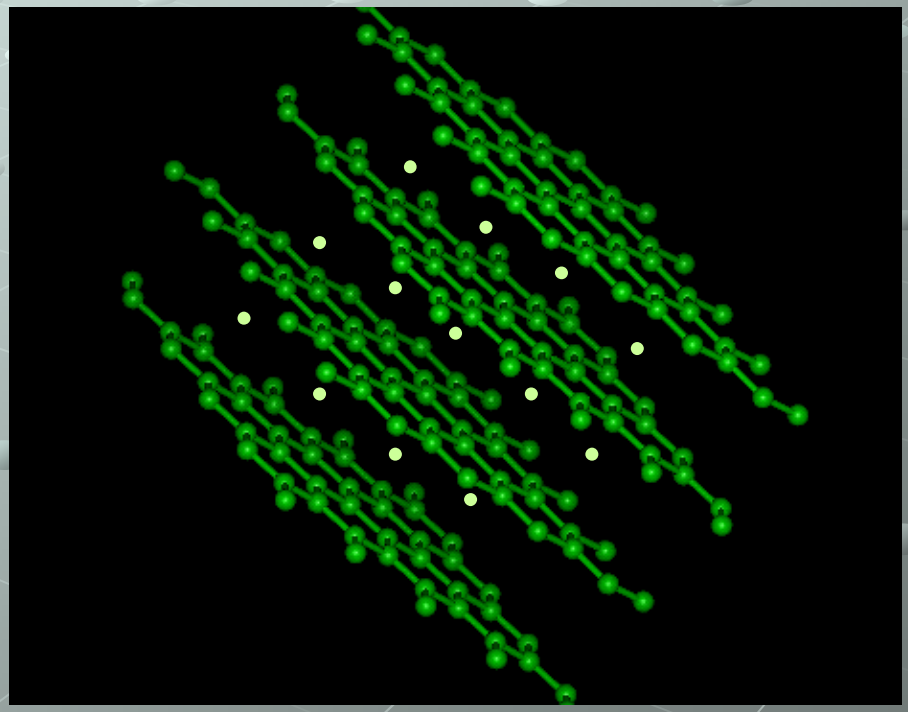
## FORME ALLOTROPICHE DEL CARBONIO (Z=6)
### (CONFIGURAZIONE ELETTRONICA ESTERNA $2s^2 2p^2$)






**Orbitale ibrido $sp^2$**

**GRAFITE**

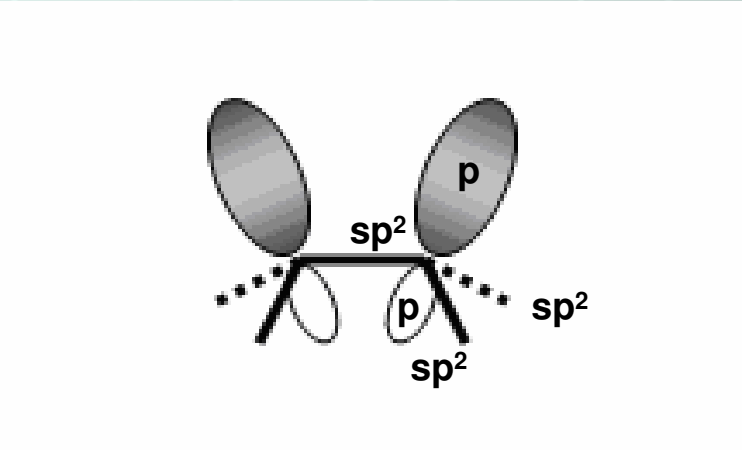


**Legami σ nel piano,**
**legami π e forze di Van der Waals tra i piani**

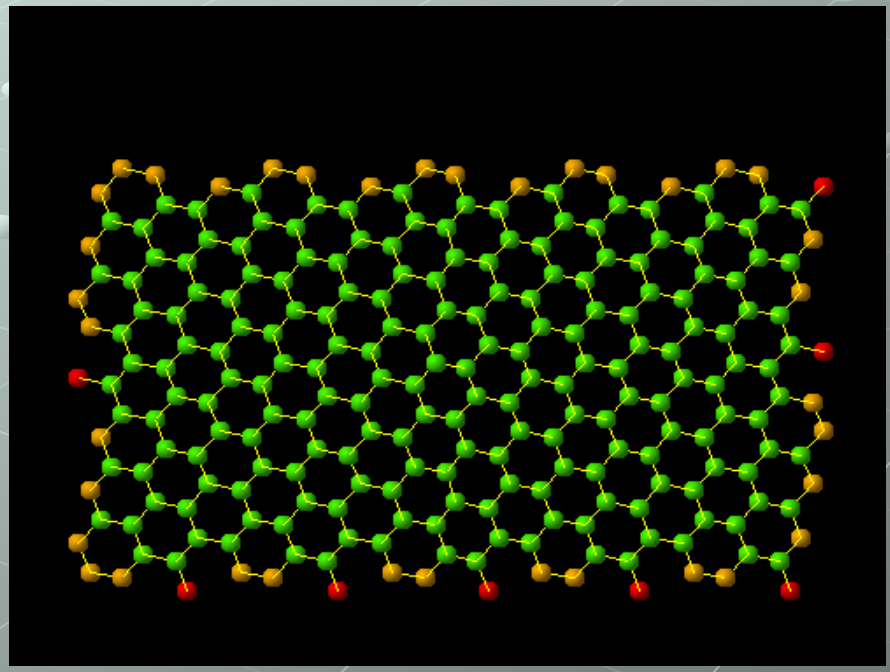
# STRUTTURA E PROPRIETÀ DEI CNT

## FORME ALLOTROPICHE DEL CARBONIO (Z=6)
(CONFIGURAZIONE ELETTRONICA ESTERNA $2s^2 2p^2$)

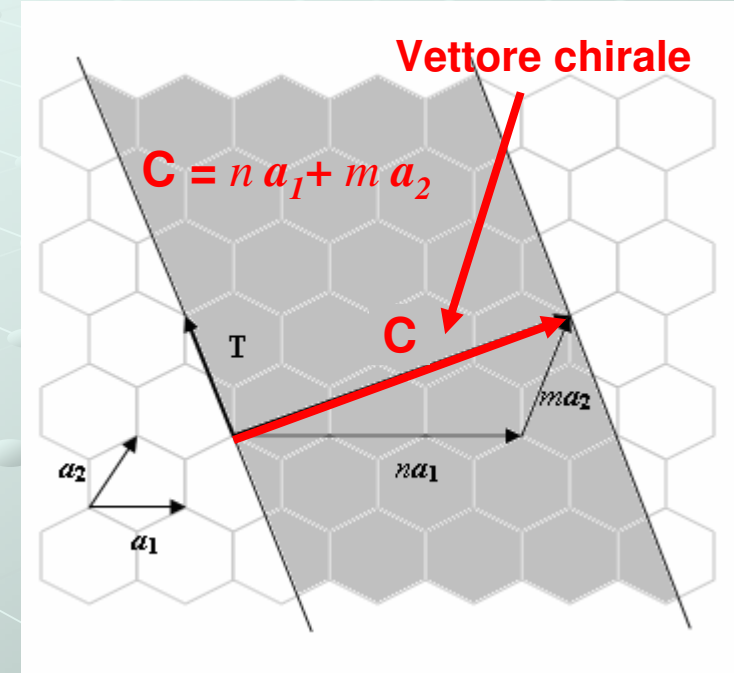
**NANOTUBO DI CARBONIO**




**Orbitale ibrido $sp^2$ deformato**

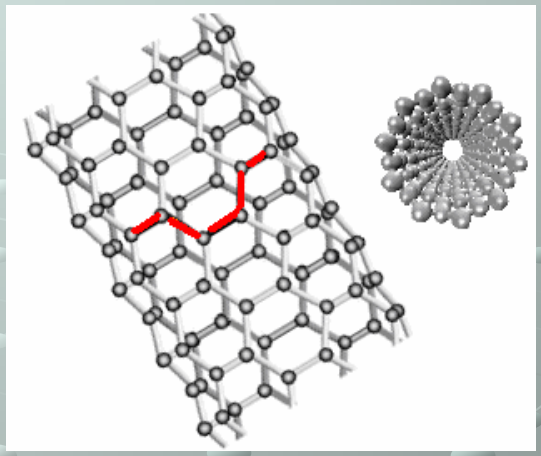


# STRUTTURA E PROPRIETÀ DEI CNT

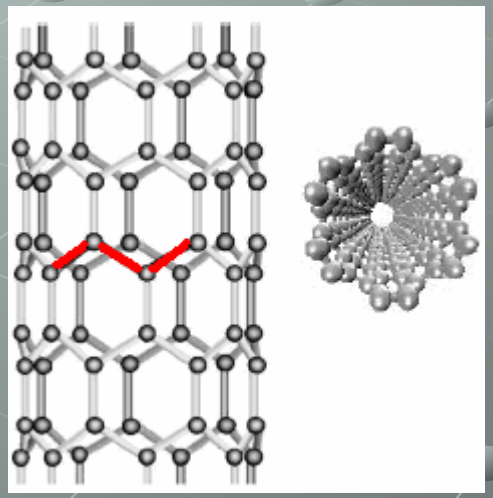



$$D = \frac{|C|}{\pi} = \frac{a\sqrt{n^2 + nm + m^2}}{\pi}$$

**Diametro dei tubi**



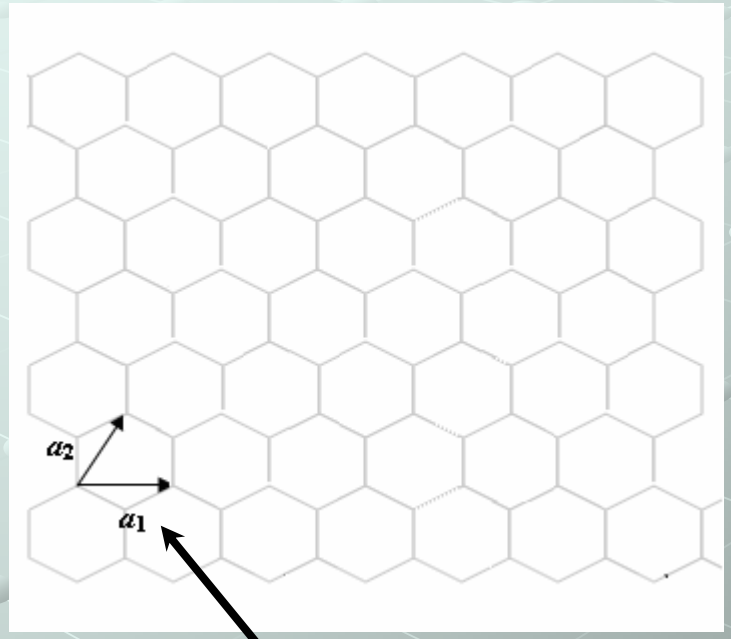
**Zig–zag ($n$, $n$)**



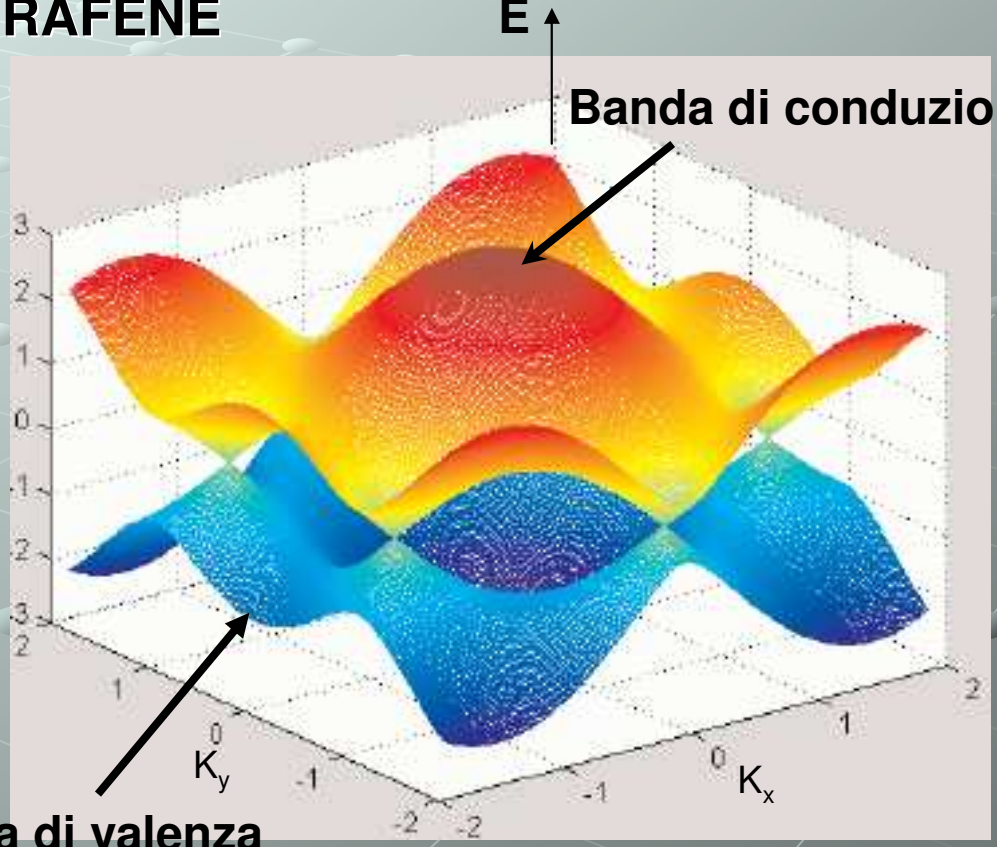
**Armchair ($n$,0)**

# PROPRIETÀ ELETTRONICHE

**GRAFENE**



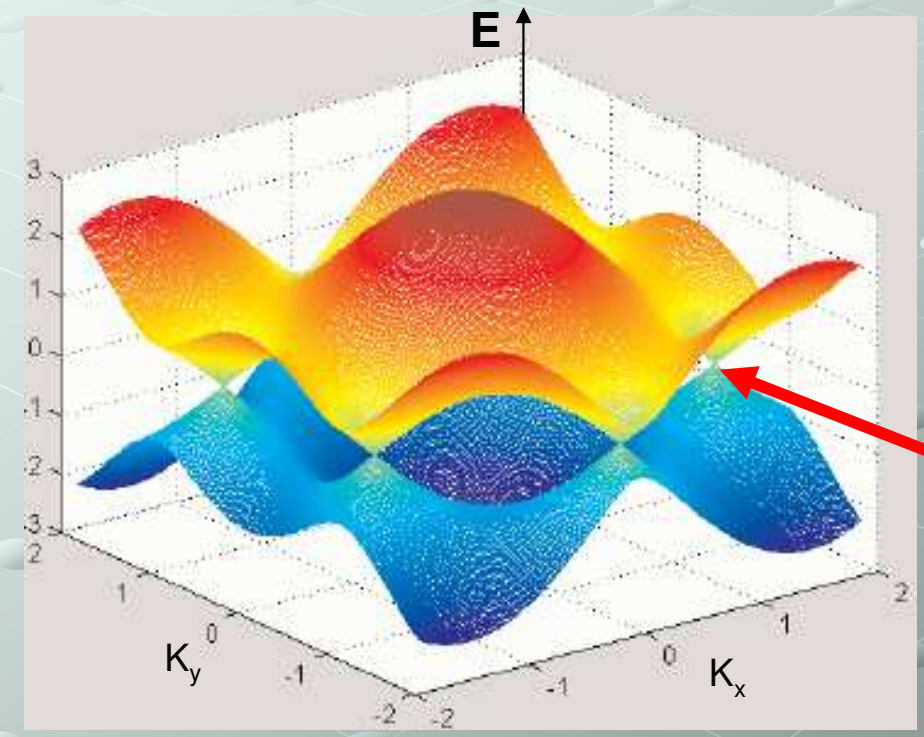

$a$ = 0.246 nm

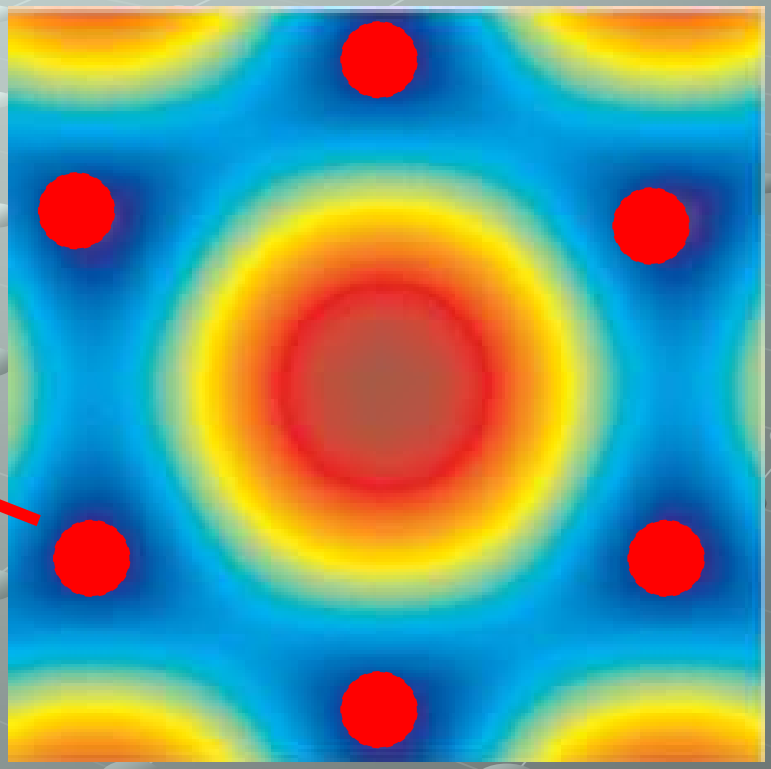



**Struttura a bande del grafene**

# PROPRIETÀ ELETTRONICHE

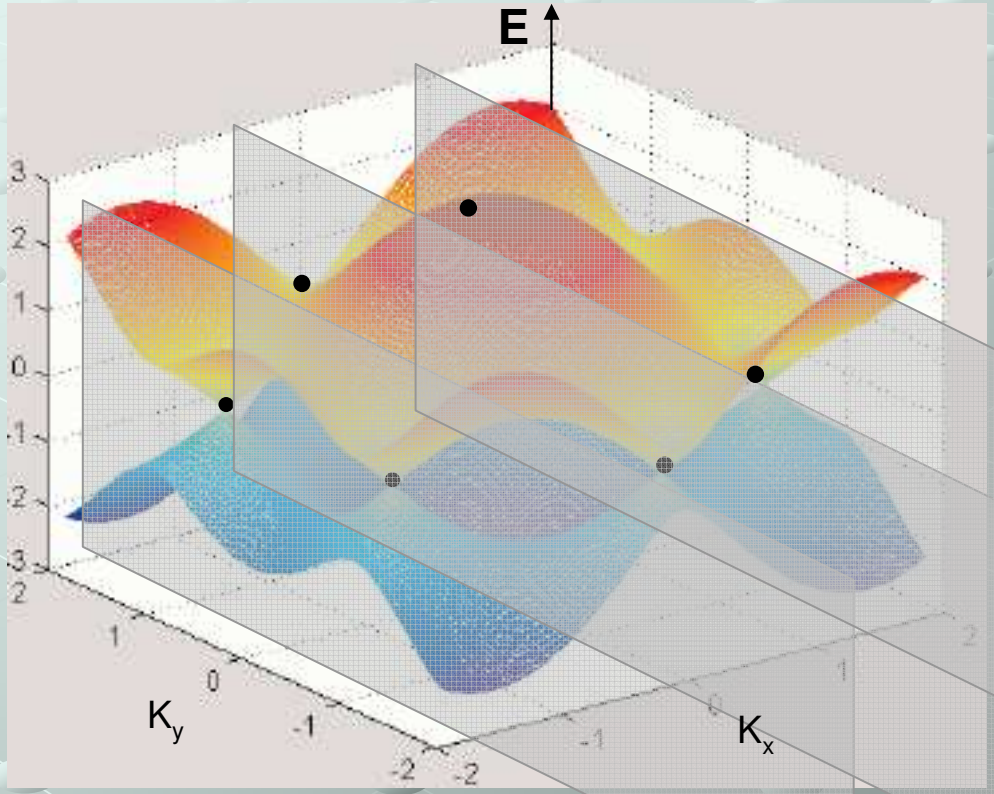
**GRAFENE**

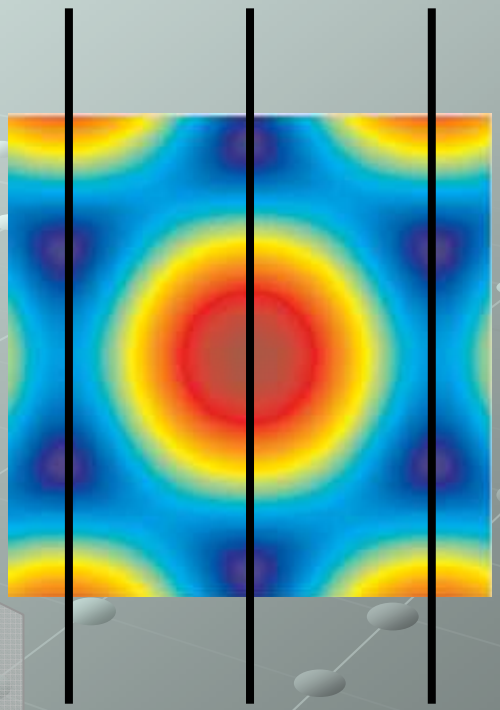


# PROPRIETÀ ELETTRONICHE

## CNT METALLICI



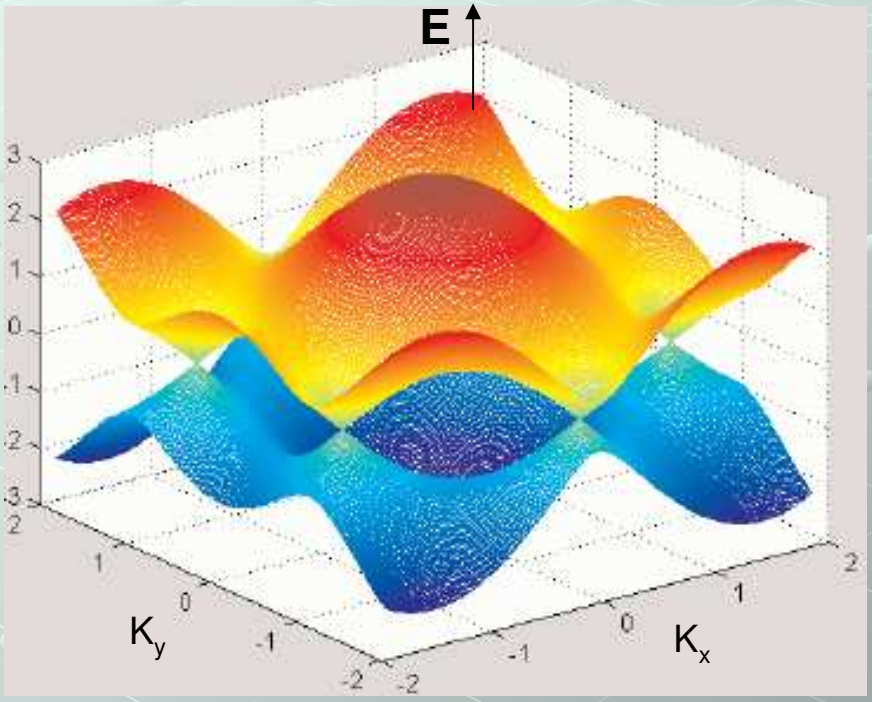
Linee di quantizzazione

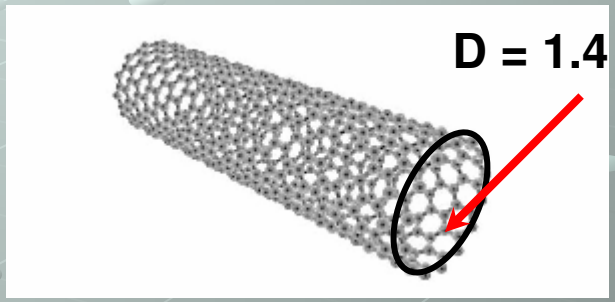
***Condizione di metallicità***

$n - m = 3q$ $q$ intero

# PROPRIETÀ ELETTRONICHE

## CNT SEMICONDUTTORI



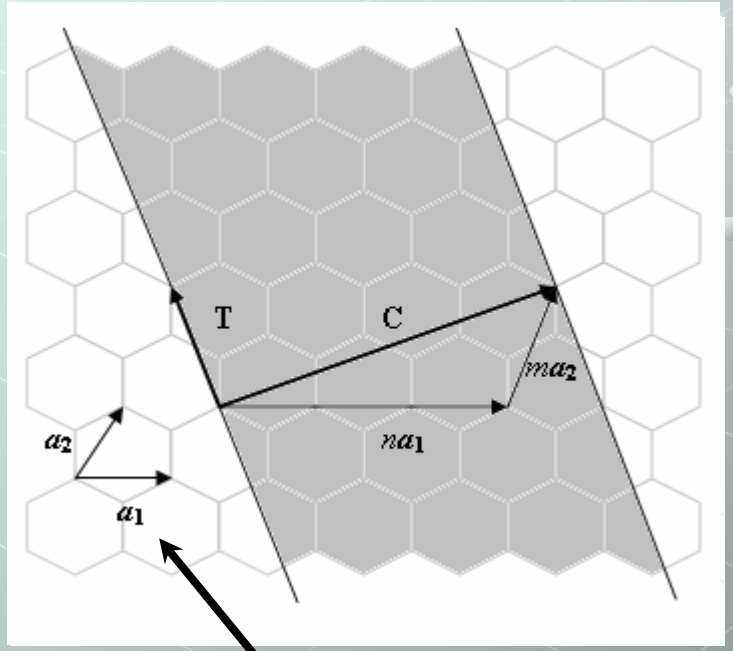

**Energia di gap ~ 1 eV**

$$\Delta E_{gap} = \frac{2a_0\gamma}{D}$$

$$\left(\gamma = 2.9\ \text{eV},\ a_0 = \frac{\hbar}{m_e e^2}\right)$$

# PROPRIETÀ ELETTRONICHE

$$\Delta k = \frac{2\pi}{\sqrt{3}\, a\, |C|} = \frac{2}{D}$$

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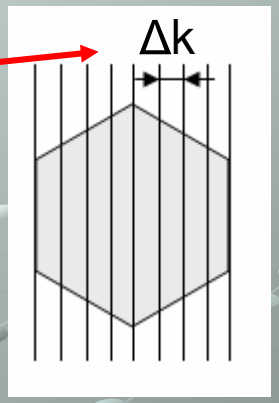
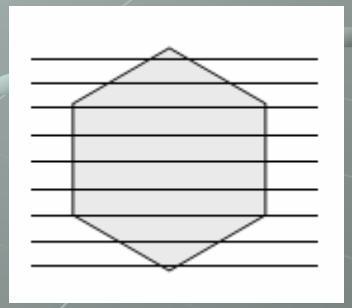
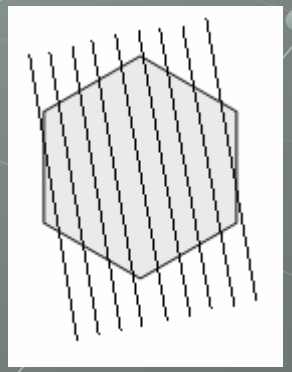



**Armchair**



**Zig-zag**



**Chirale**

# PROPRIETÀ ELETTRONICHE

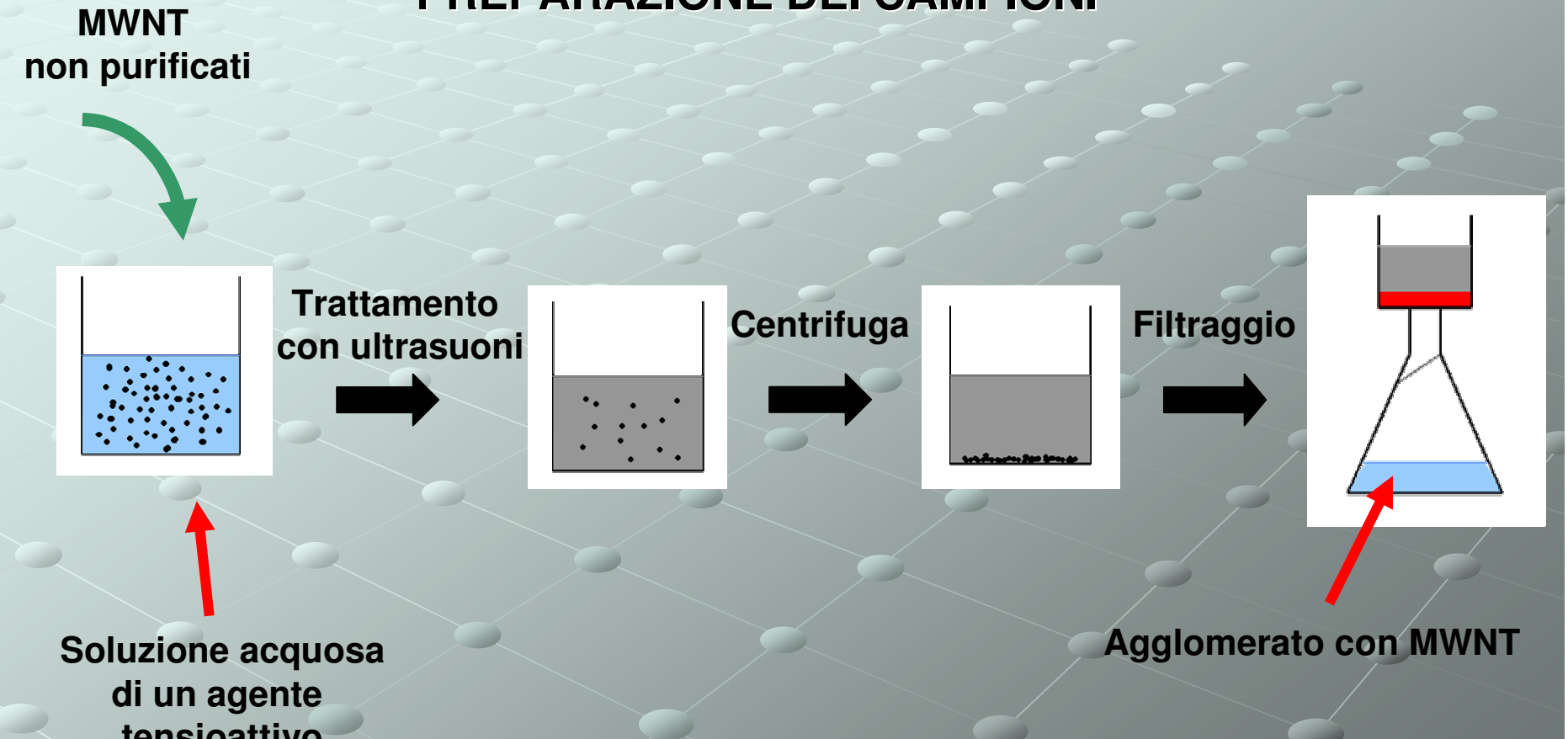
- **SWNT**
  - Armchair → **metallici**
  - Zig-zag e chirali (n,m) → **metallici se $n - m = 3q$ , $q$ intero**
- **MWNT (D>> )** → **prevalentemente metallici e semimetallici.**
- **In opportune condizioni la conduzione nei CNT può essere di tipo balistico.**

# ATTIVITÀ SPERIMENTALI

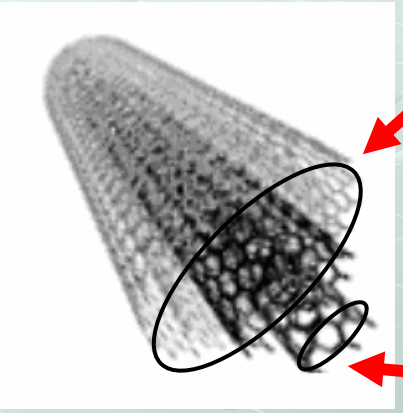
- **R(T) di film di MWNT**
- **Conduttività elettrica di campioni PE/MWNT**
- **Emissione di campo da MWNT allineati**

# PROPRIETÀ ELETTRICHE DI MWNT
# BUCKY PAPER

## PREPARAZIONE DEI CAMPIONI

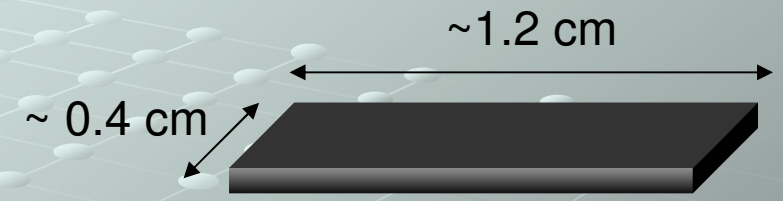


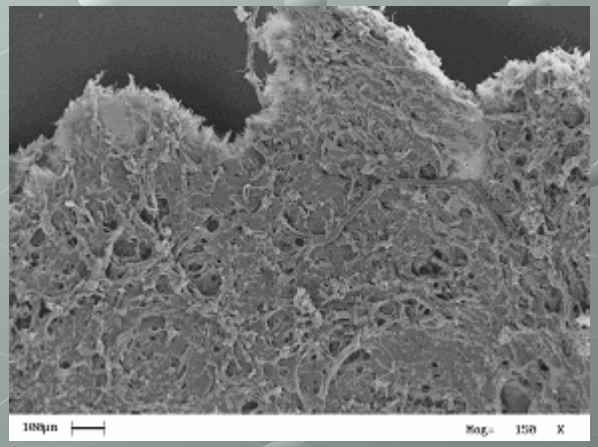
# PROPRIETÀ ELETTRICHE DI MWNT
# BUCKY PAPER



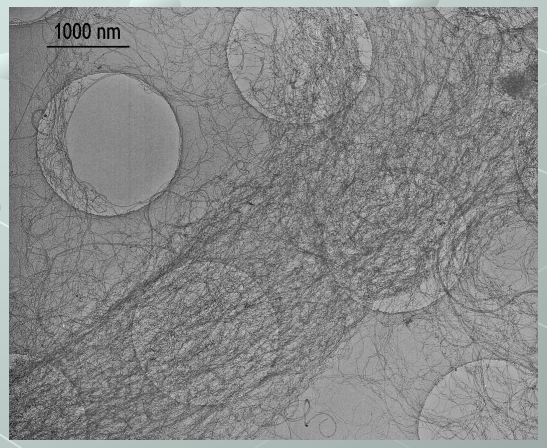
D ~ 15 nm

D = 5 - 8 nm



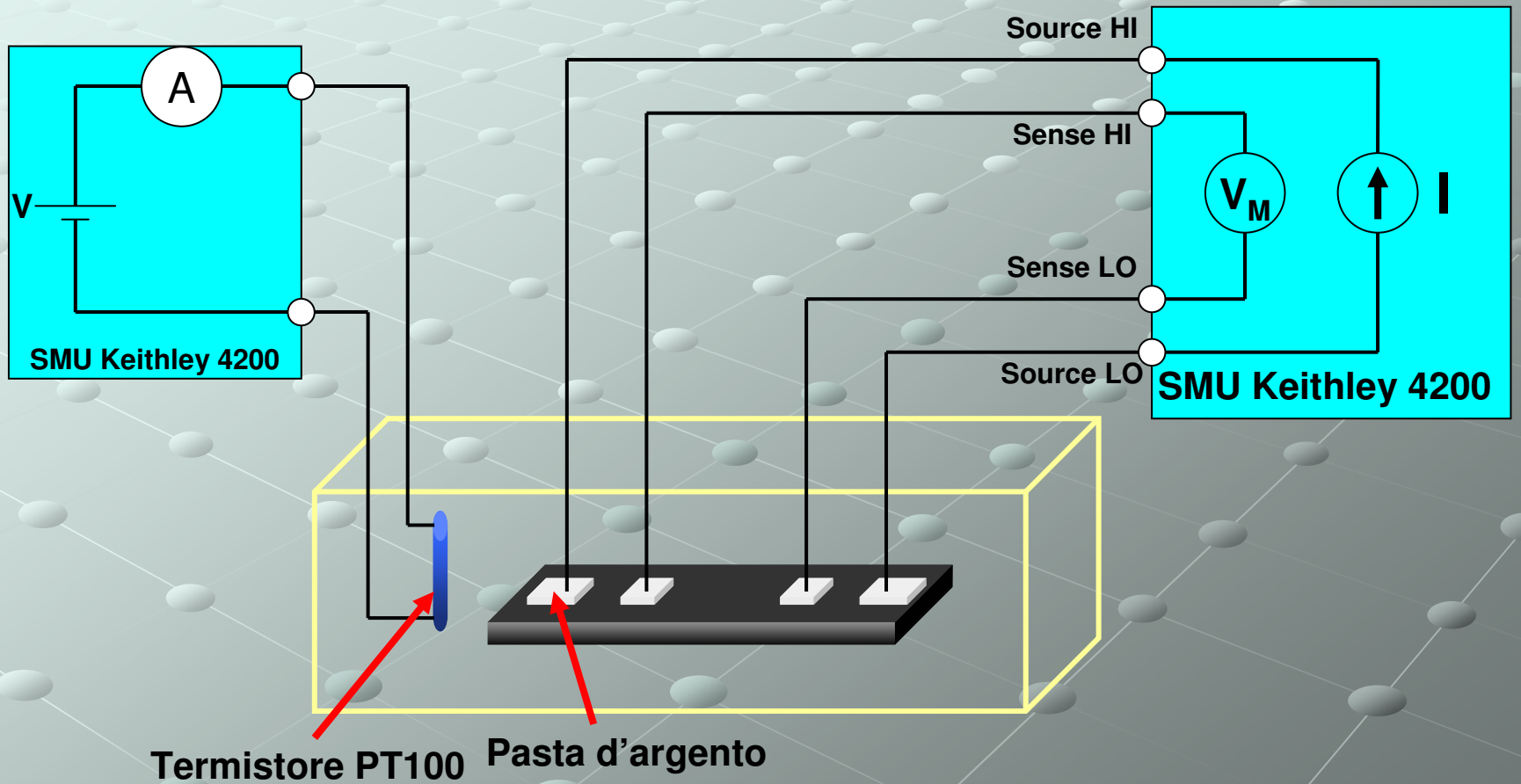
MWNT bucky paper




MWNT

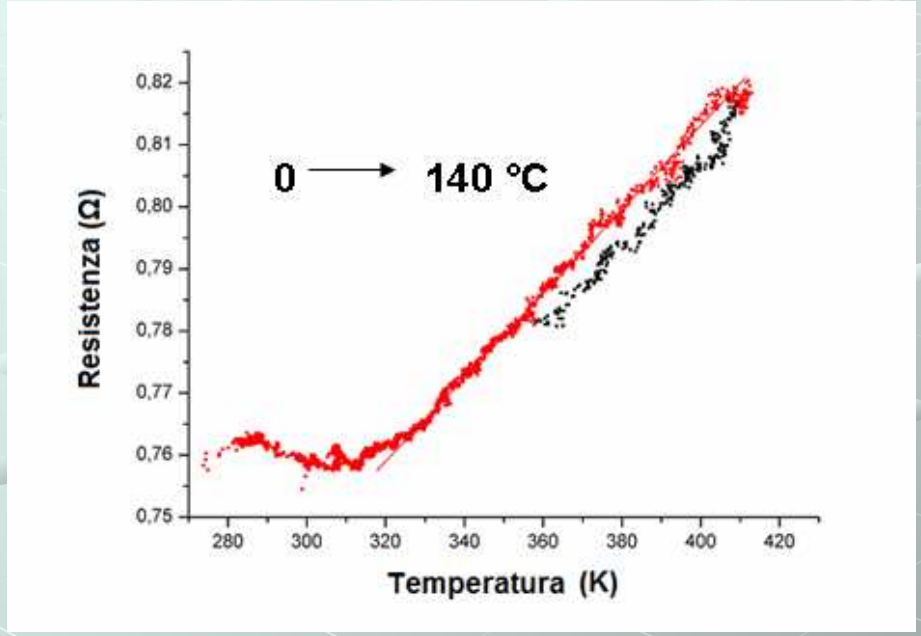
# PROPRIETÀ ELETTRICHE DI MWNT BUCKY PAPER

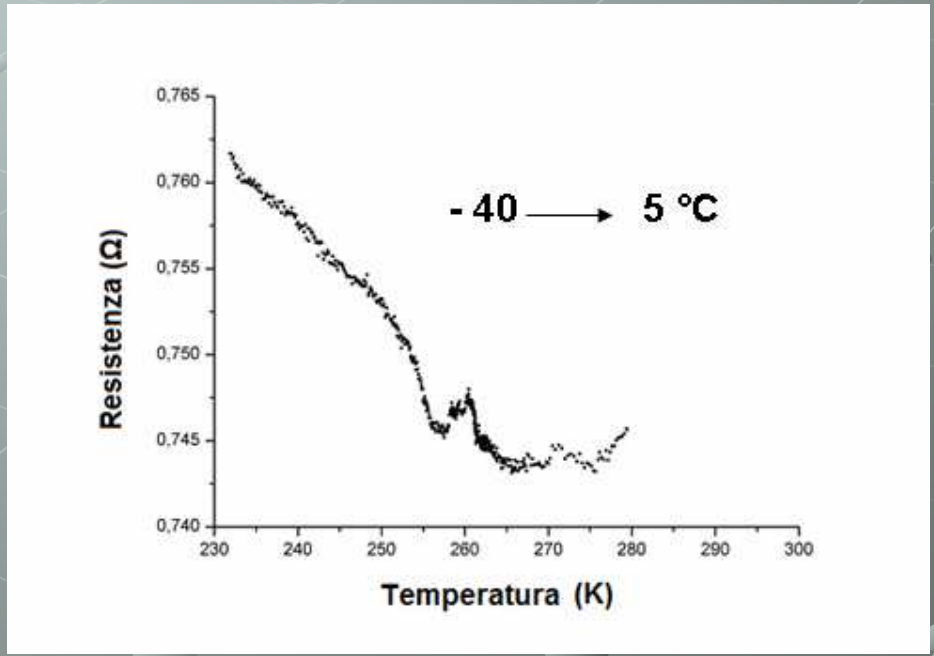
## APPARATO DI MISURA



# PROPRIETÀ ELETTRICHE DI MWNT
# BUCKY PAPER

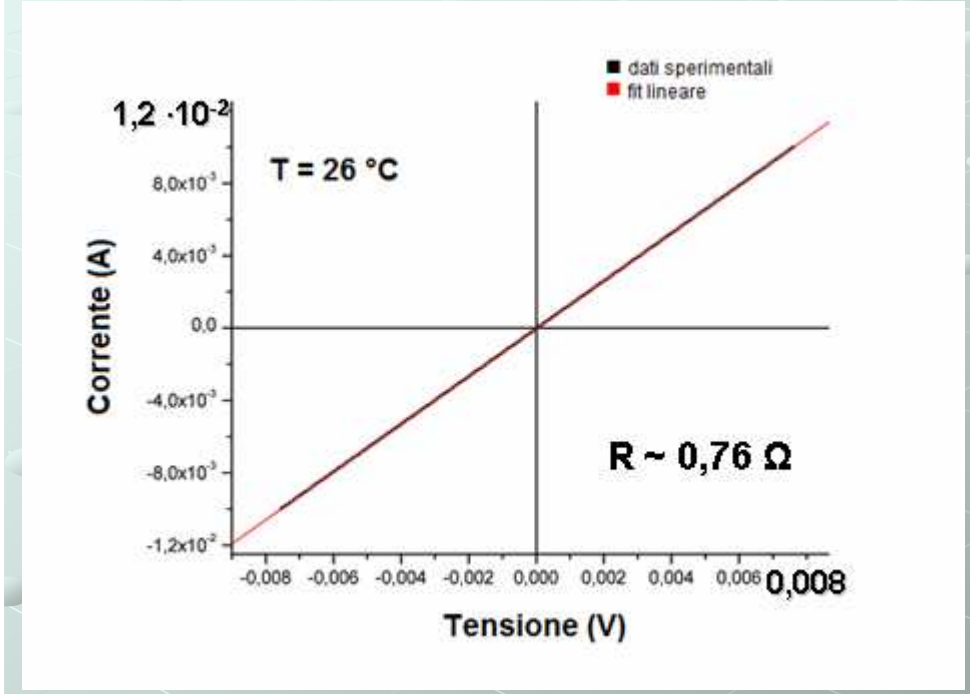
## RESISTENZA vs TEMPERATURA

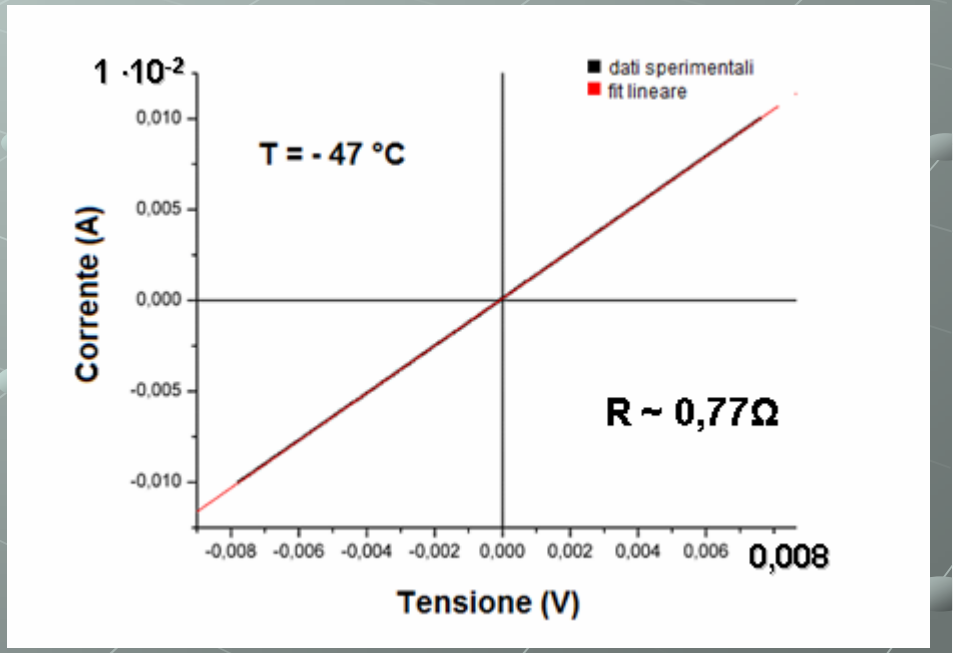


# PROPRIETÀ ELETTRICHE DI MWNT
# BUCKY PAPER

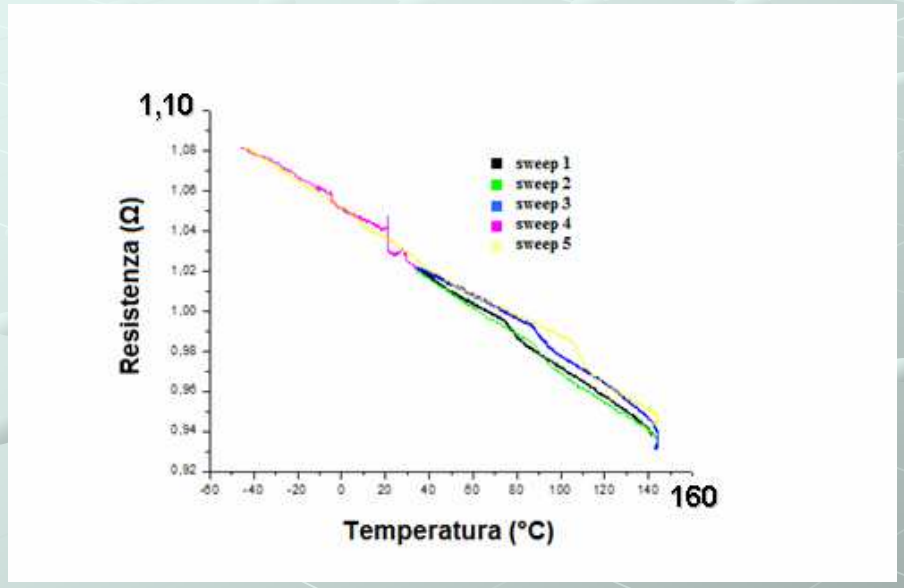
## CARATTERISTICA I-V

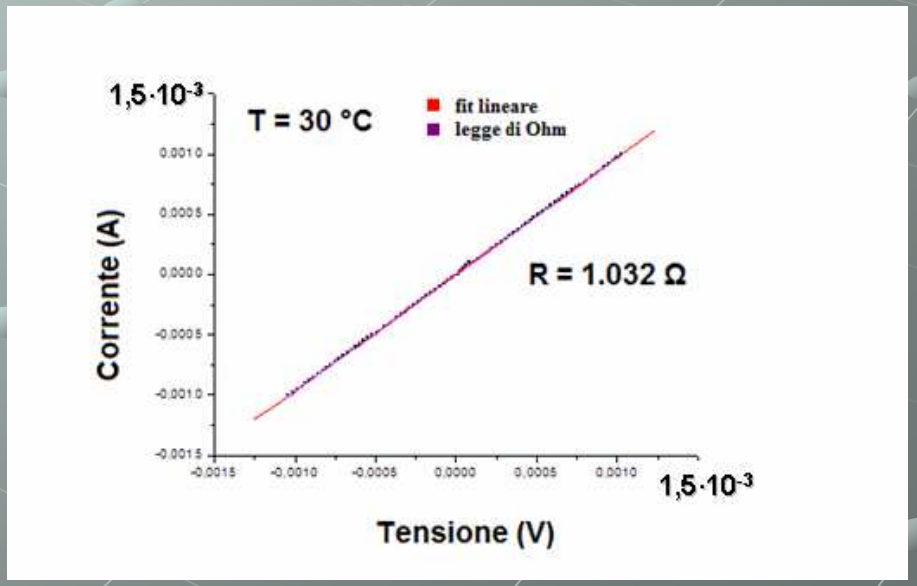


# PROPRIETÀ ELETTRICHE DI MWNT BUCKY PAPER

## RESISTENZA vs TEMPERATURA

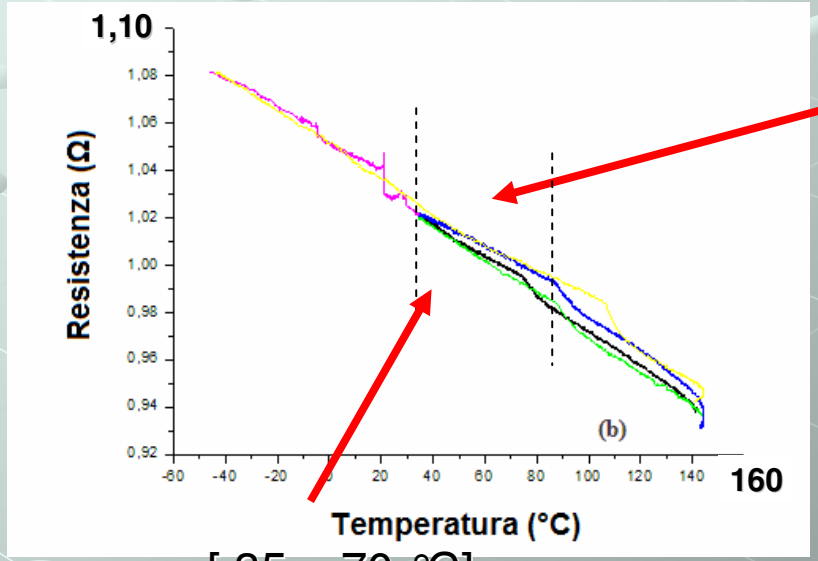


# PROPRIETÀ ELETTRICHE DI MWNT
# BUCKY PAPER

## STIMA DEL COEFFICIENTE DI TEMPERATURA DELLA RESISTENZA
## (Temperature Coefficient Resistance)

$$R(T) = R(T_0)\left[1 + \alpha (T-T_0)\right]$$ α coefficiente di temperatura




[ 35 – 70 °C]

Fit lineare $R = A + m\,(T-T_0)$

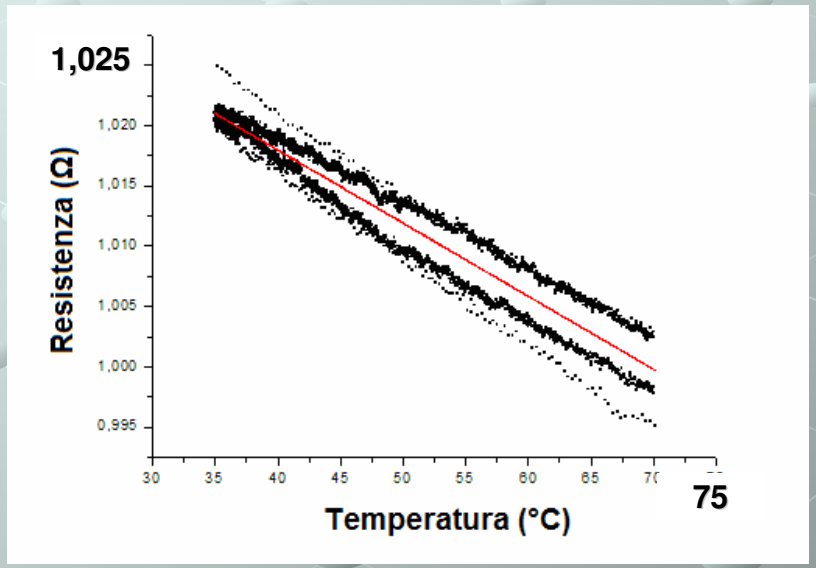
$R(T0) - \alpha\, T_0\, R\,(T_0)$

α R(To)

# PROPRIETÀ ELETTRICHE DI MWNT BUCKY PAPER

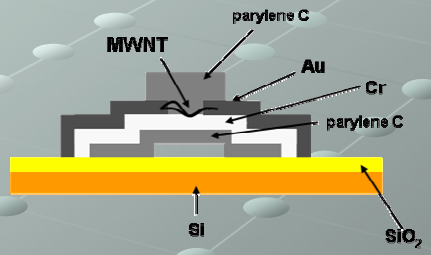
## IL NOSTRO DISPOSITIVO

**TCR ~ -0.054 – -0.065 % $C^{-1}$**

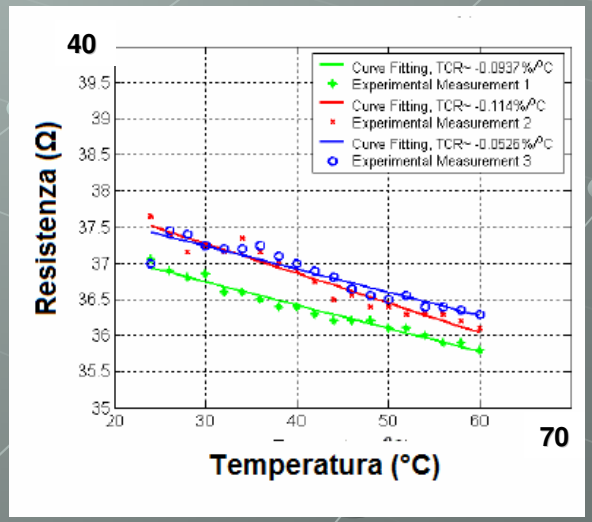



## FUNG ET AL.

*(Nanotechnology, 15, S672–S677 (2004))*




**TCR ~ -0.05 – -0.07 % $°C^{-1}$**



# ATTIVITÀ SPERIMENTALI

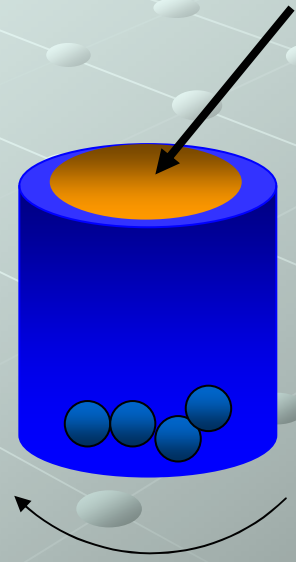
- R(T) di film di MWNT
- **Conduttività elettrica di campioni PE/MWNT**
- Emissione di campo da MWNT

# PROPRIETÀ ELETTRICHE DI CAMPIONI PE/MWNT

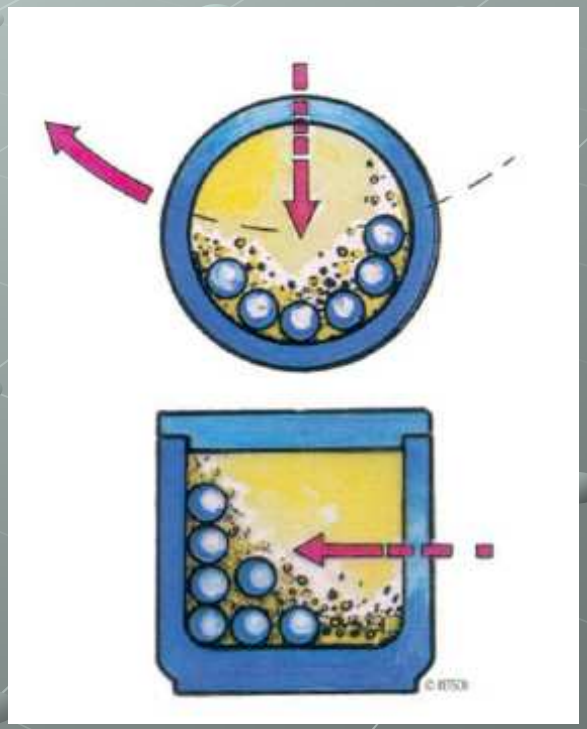
## DISPERSIONE DEI MWNT

### BALL MILLING AD ALTA ENERGIA (HIGH ENERGY BALL MILLING)

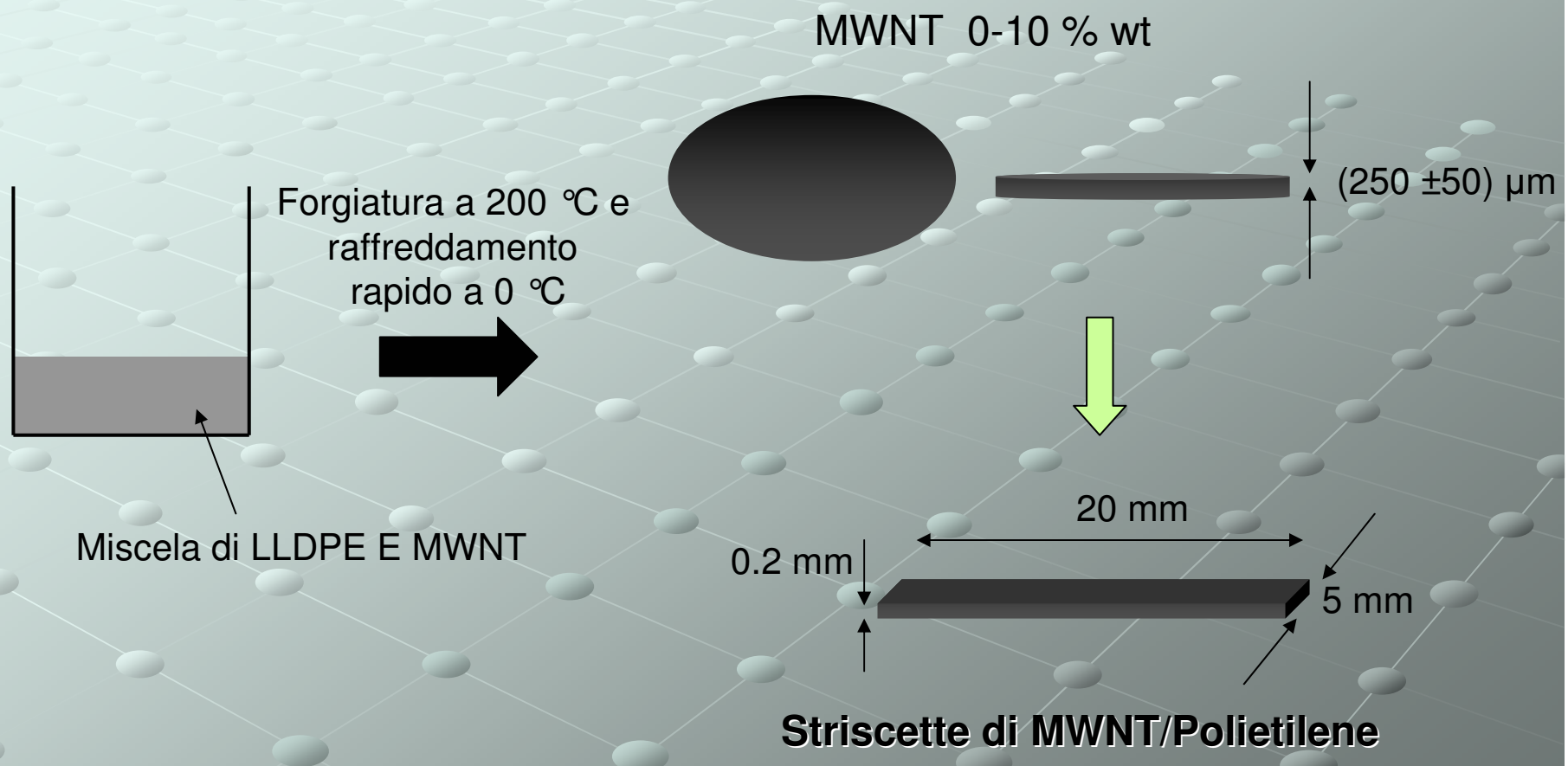
Polveri di MWNT e polietilene



**Velocità: 580 rpm**

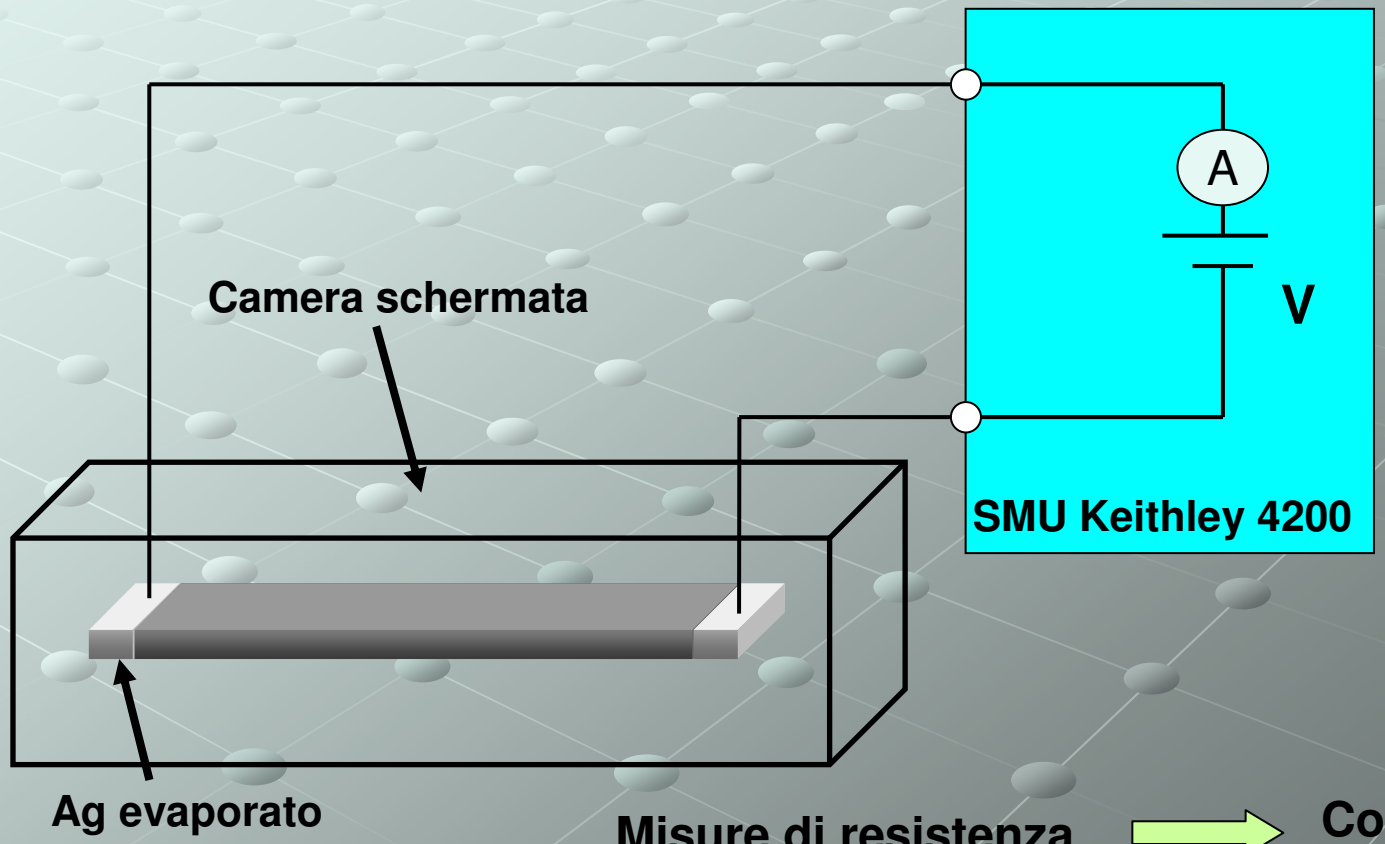


# PROPRIETÀ ELETTRICHE DI CAMPIONI PE/MWNT



# PROPRIETÀ ELETTRICHE DI CAMPIONI PE/MWNT

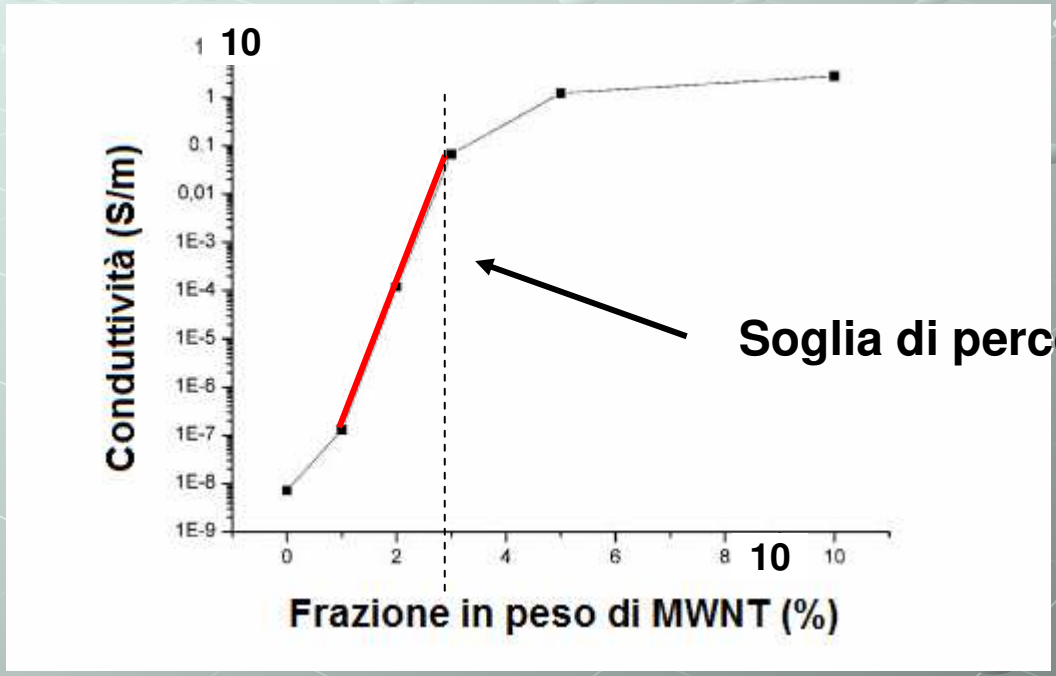
## APPARATO DI MISURA




Misure di resistenza → Conduttività

# PROPRIETÀ ELETTRICHE DI CAMPIONI PE/MWNT

**RESISTENZA vs FRAZIONE IN PESO DI DI MWNT**



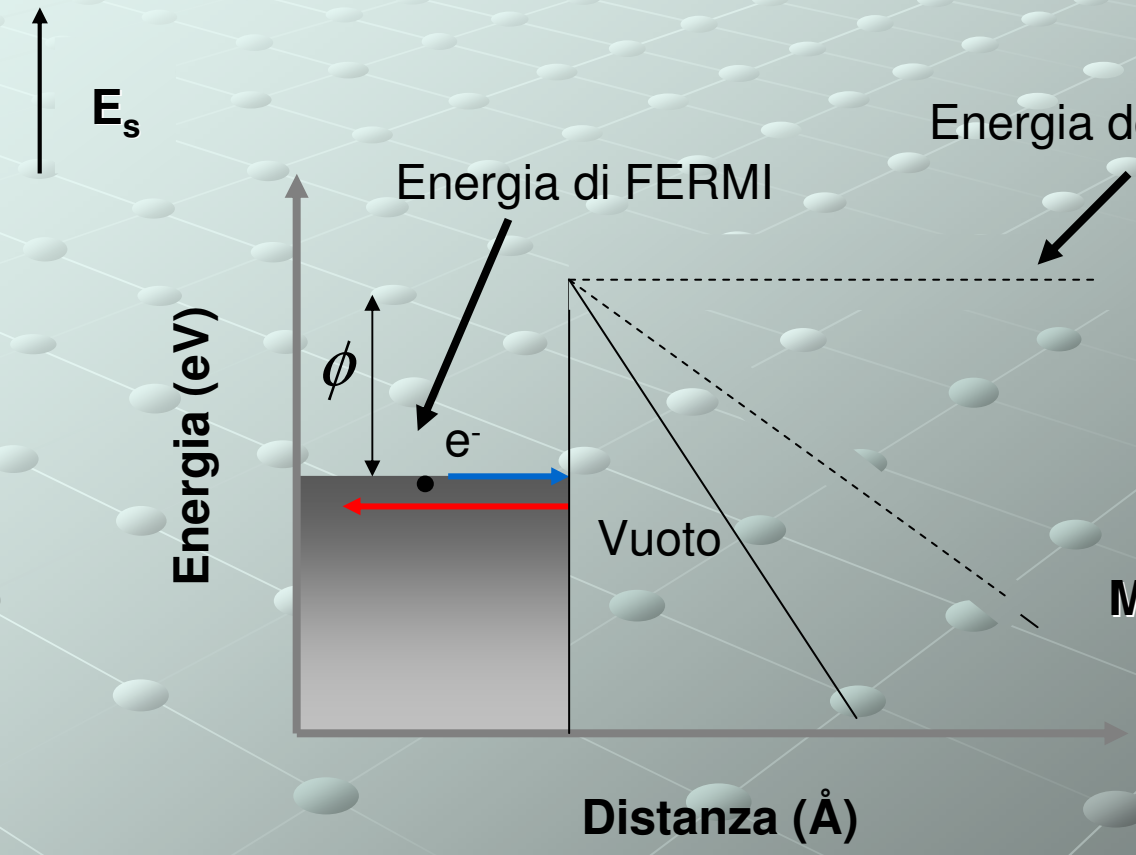

**Soglia di percolazione ~3 % wt**

# ATTIVITÀ SPERIMENTALI

- R(T) di film di MWNT
- Conduttività elettrica di campioni PE/MWNT
- **Emissione di campo da MWNT allineati**

# EMISSIONE DI CAMPO DA MWNT PARZIALMENTE ALLINEATI

## EMISSIONE DI CAMPO



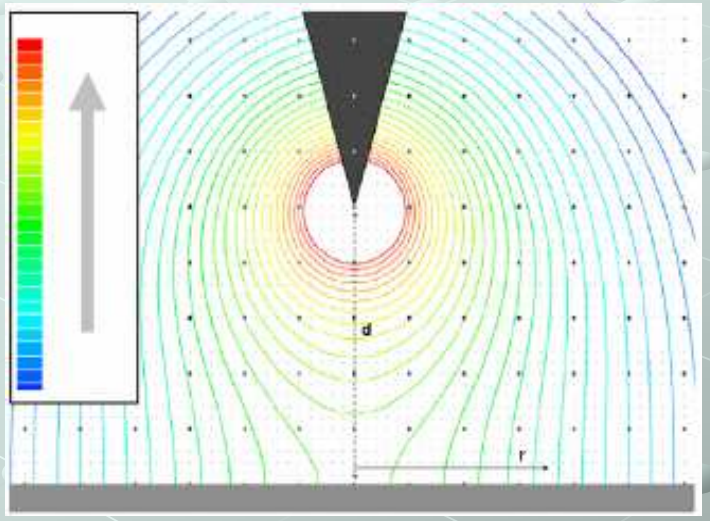

$$I = S\, a \frac{E_s^{\,2}}{\phi} e^{\left(-b\frac{\phi^{\frac{3}{2}}}{E_s}\right)}$$

**Modello di Fowler-Nordheim**

# EMISSIONE DI CAMPO DA MWNT PARZIALMENTE ALLINEATI

**EMISSIONE DI CAMPO**

**$E_S$~ 50 – 100 KV/µm**



**D = 0.6 – 2 nm**

**D = 15 – 20 nm**

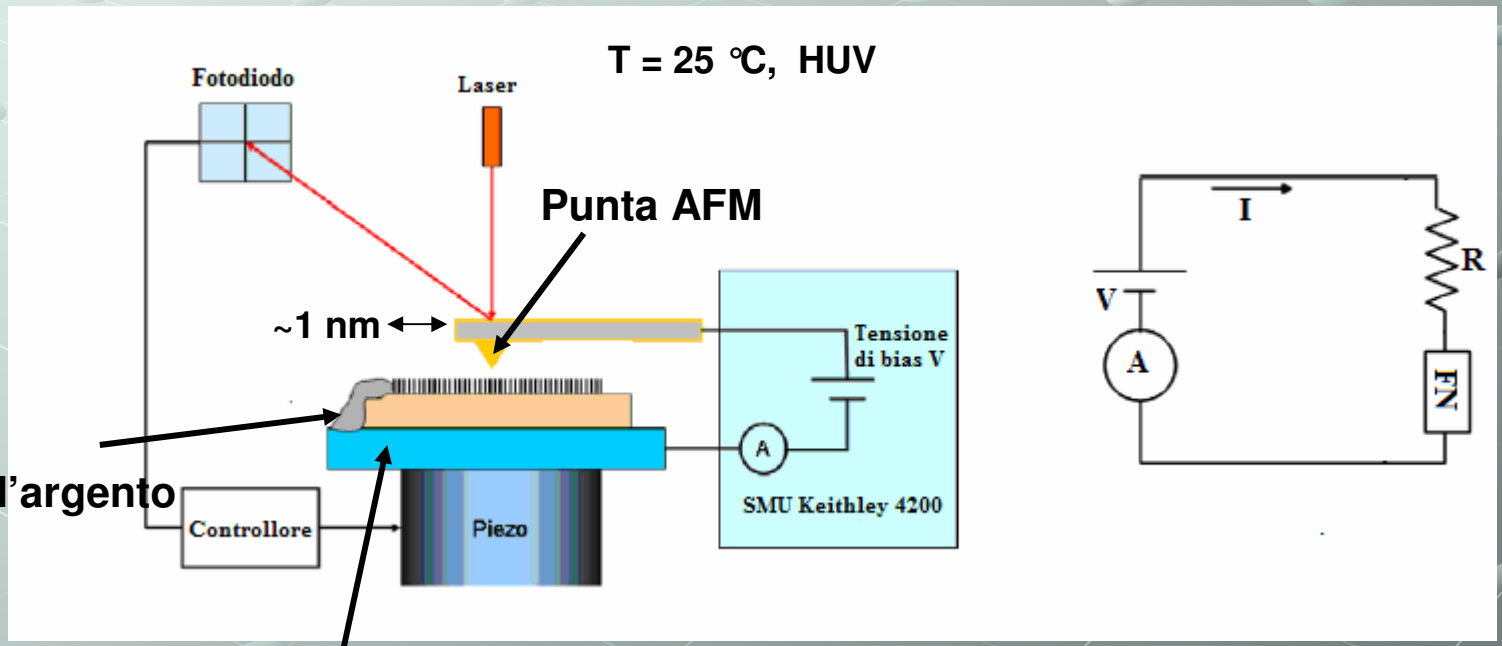
SWNT

MWNT

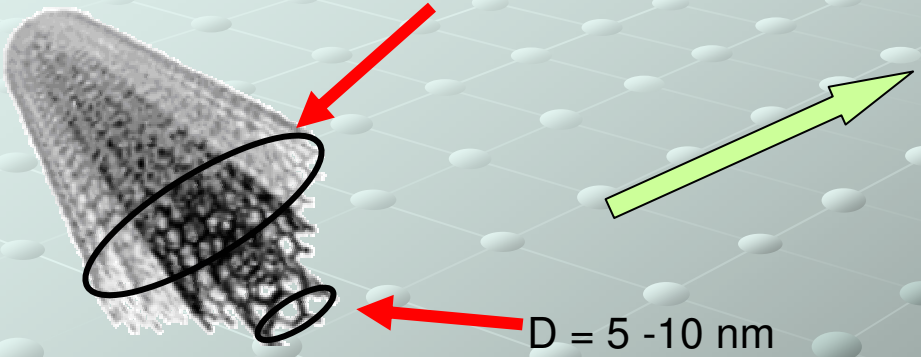
**$E_S$~ 1-3 KV/µm**

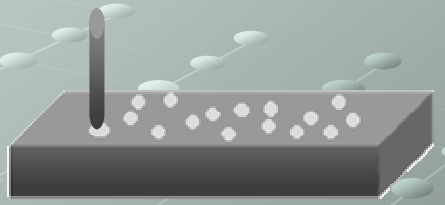
# EMISSIONE DI CAMPO DA MWNT PARZIALMENTE ALLINEATI

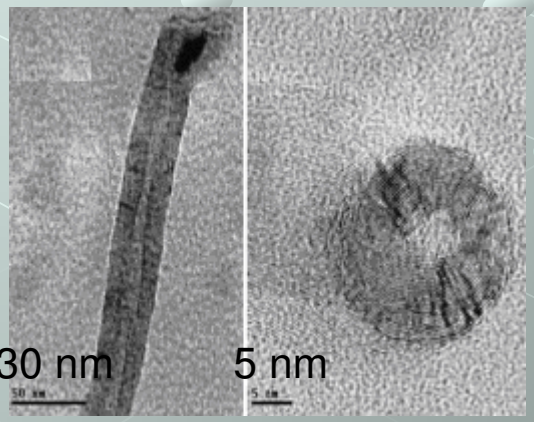
## APPARATO DI MISURA DELLA FE



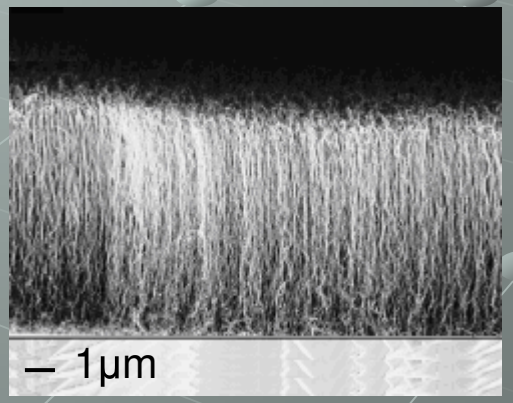
# EMISSIONE DI CAMPO DA MWNT PARZIALMENTE ALLINEATI






MWNT



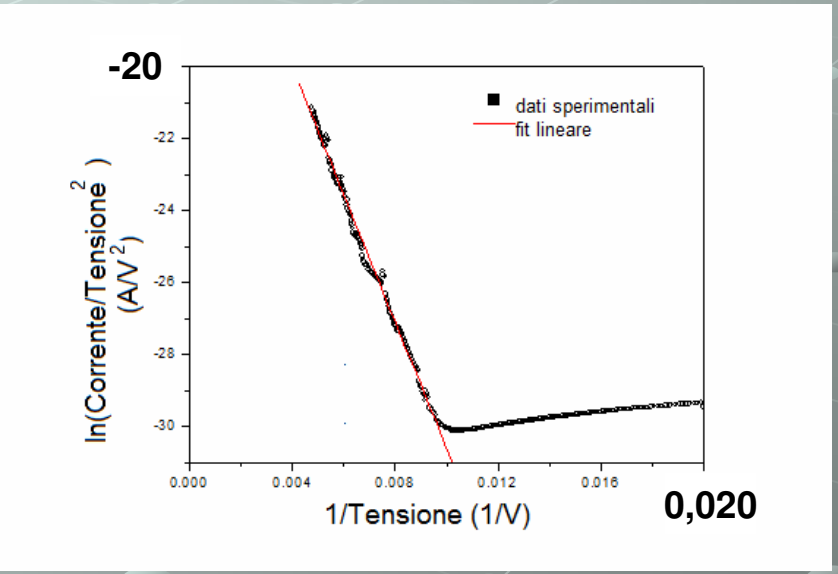

**FILM DI MWNT PARZIALMENTE ALLINEA**

# EMISSIONE DI CAMPO DA MWNT PARZIALMENTE ALLINEATI

**GRAFICO FOWLER - NORDHEIM**

$$I = S\ a\ \frac{E_s^{\ 2}}{\phi} e^{\left(-b\frac{\phi^{\frac{3}{2}}}{E_s}\right)}$$

$$\downarrow \quad E_S = \gamma \frac{V}{d}\ \frac{1}{k}$$

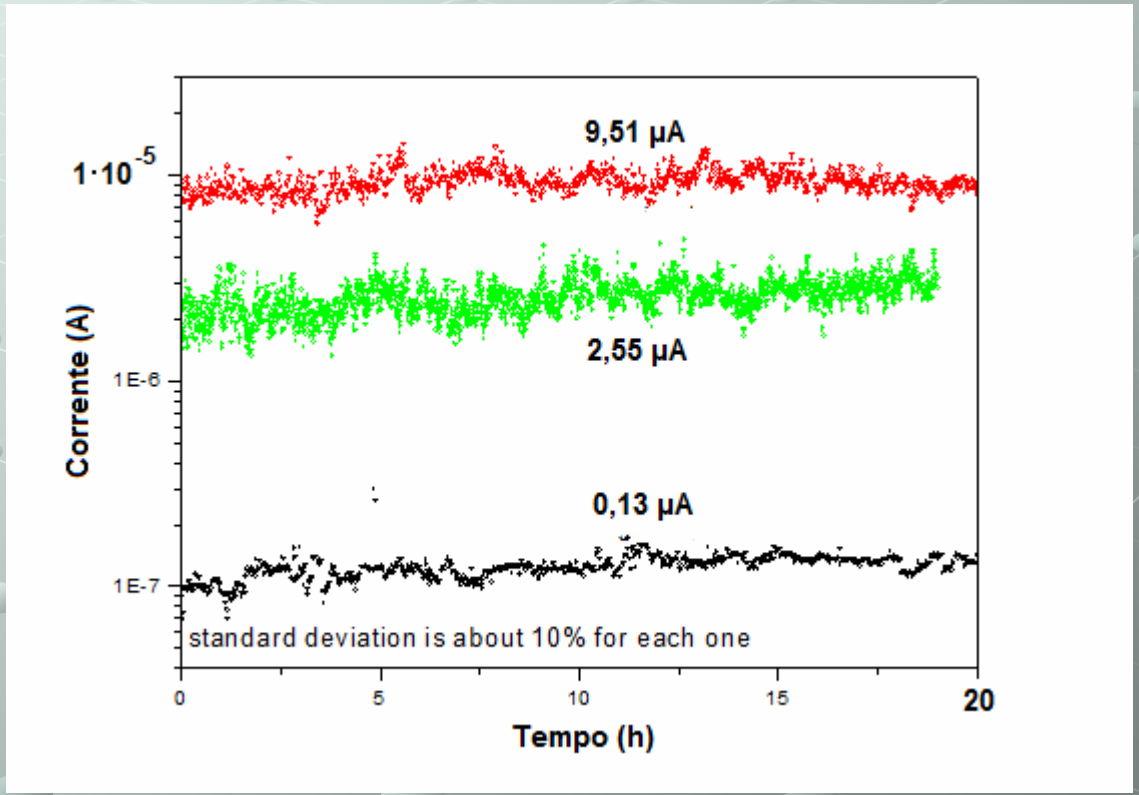



$$\ln\left(\frac{1}{V^2}\right) = \ln\left(\frac{aS\gamma^2}{\phi d^2}\right) + b\phi^{\frac{3}{2}}\frac{d}{\gamma}\left(\frac{1}{V}\right)$$

**GRAFICO FN**

# EMISSIONE DI CAMPO DA MWNT PARZIALMENTE ALLINEATI

## STABILITA'

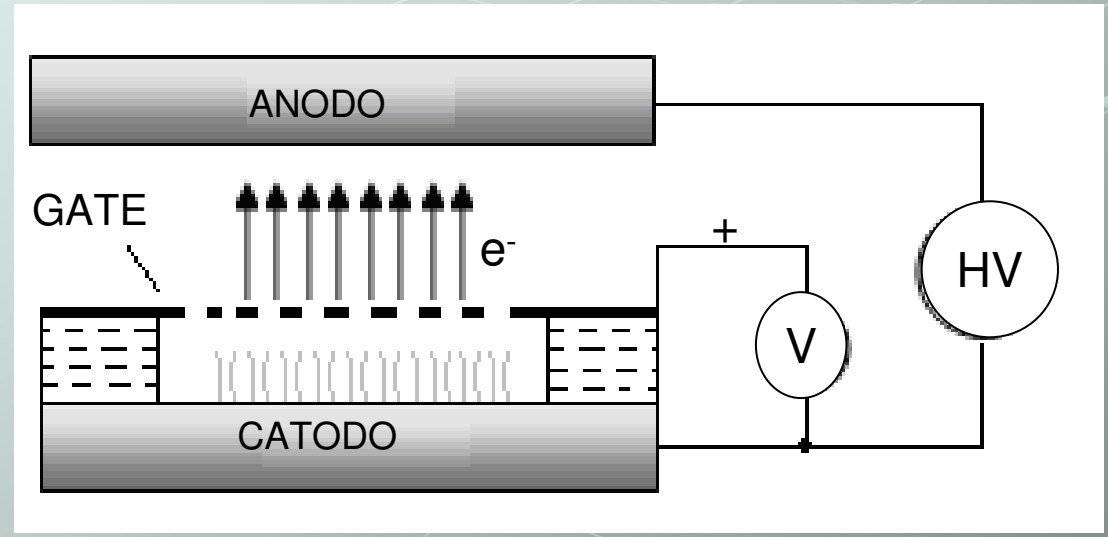


# APPLICAZIONI

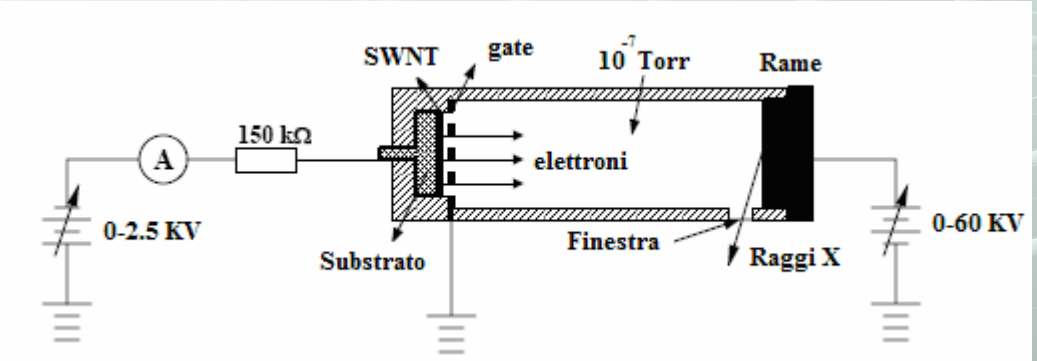
- Display e lampade ad emissione di campo
- Tubi a raggi X per la radiodiagnostica e radioterapia
- Nanoelettronica: diodi e CNTFET

# DISPOSITIVI AD EMISSIONE DI CAMPO DA CNT

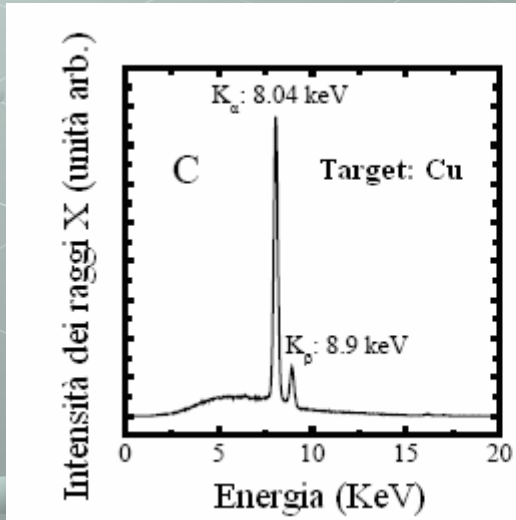
## CONFIGURAZIONE A TRIODO



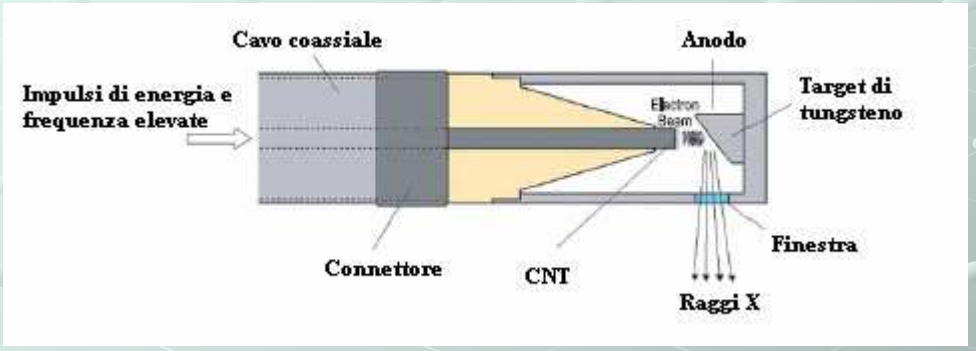
# DISPOSITIVI A EMISSIONE DI CAMPO PER LA MEDICINA




**TUBO A RAGGI X**
**PER LA RADIODIAGNOSTICA**

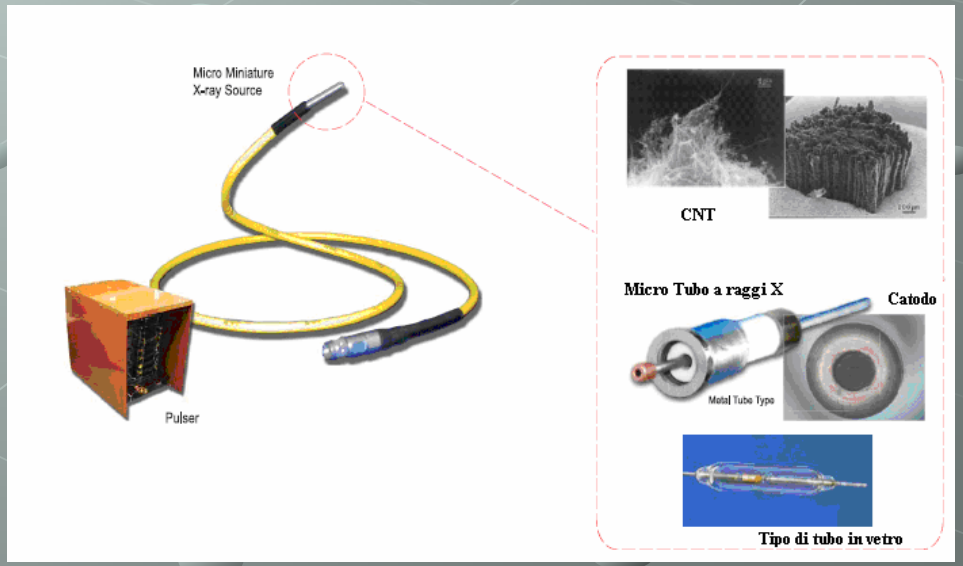



# DISPOSITIVI A EMISSIONE DI CAMPO PER LA MEDICINA



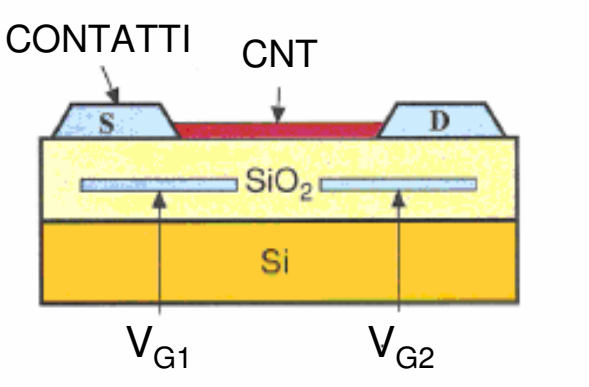

| | |
|---|---|
| Energia del fascio | Variabile in modo continuo (60 KeV max) |
| Corrente massima del fascio | 1 kA max |
| Durata dgli impulsi | 20 ns |
| Diametro del tubo a raggi X | < 5mm |

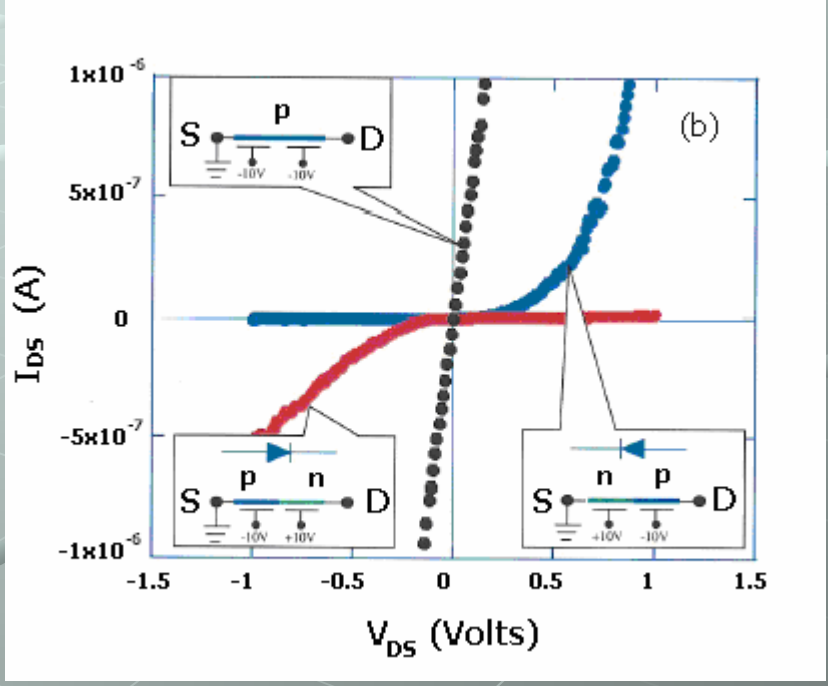
## TUBO A RAGGI X MINIATURIZZATO PER LA RADIOTERAPIA



# NANOELETTRONICA

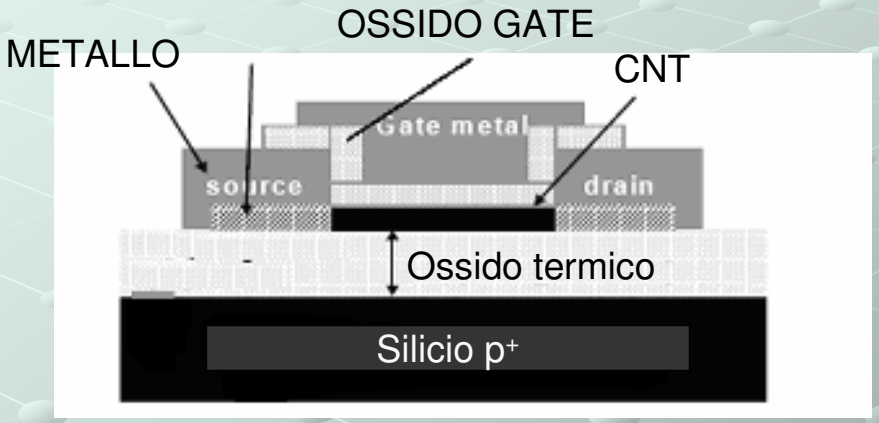
## DIODO A CNT

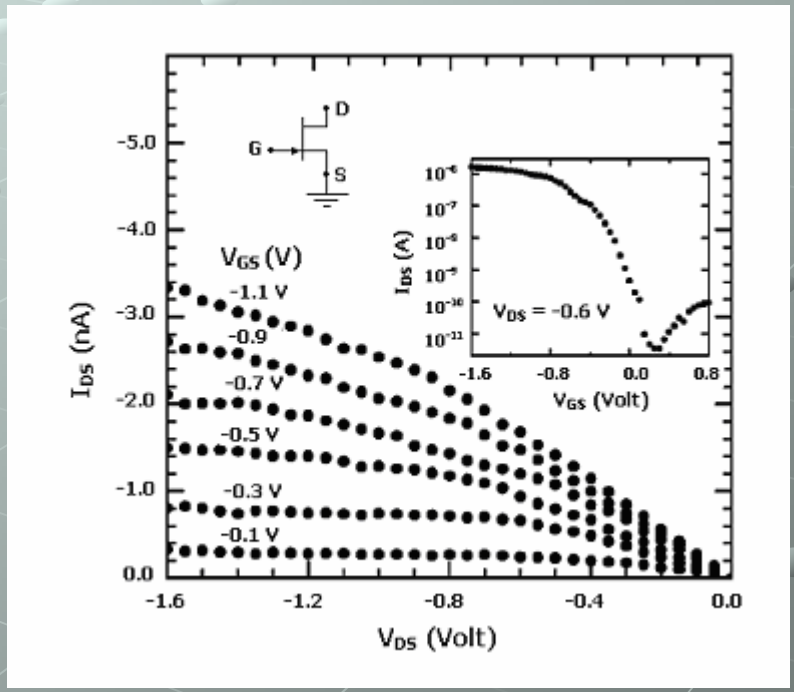


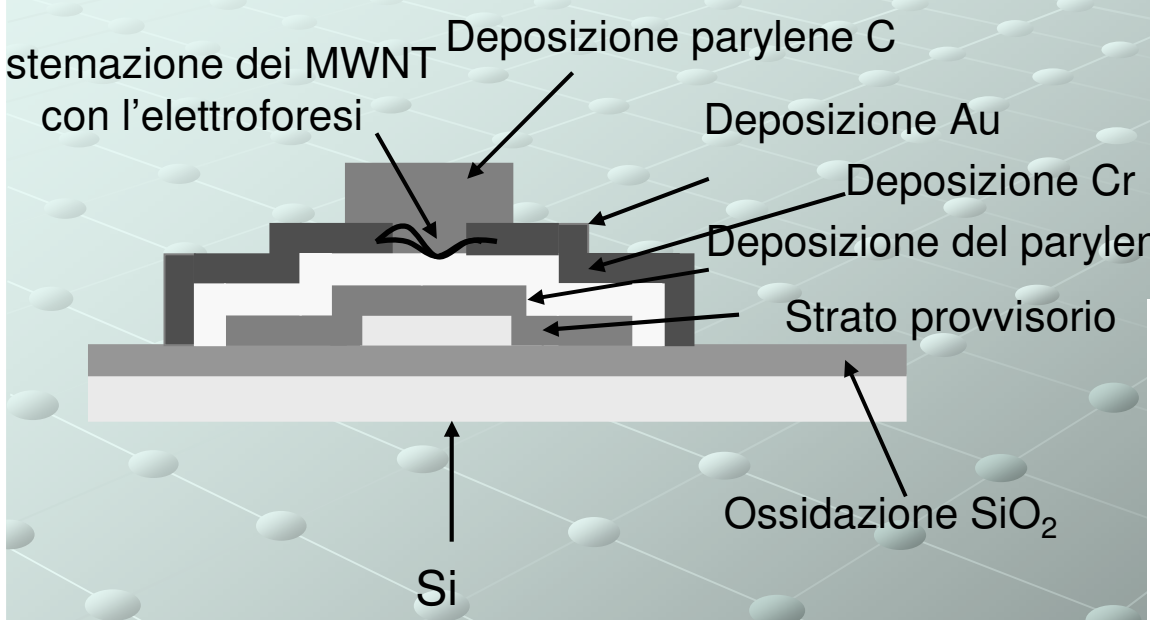
# NANOELETTRONICA

## CNT FET

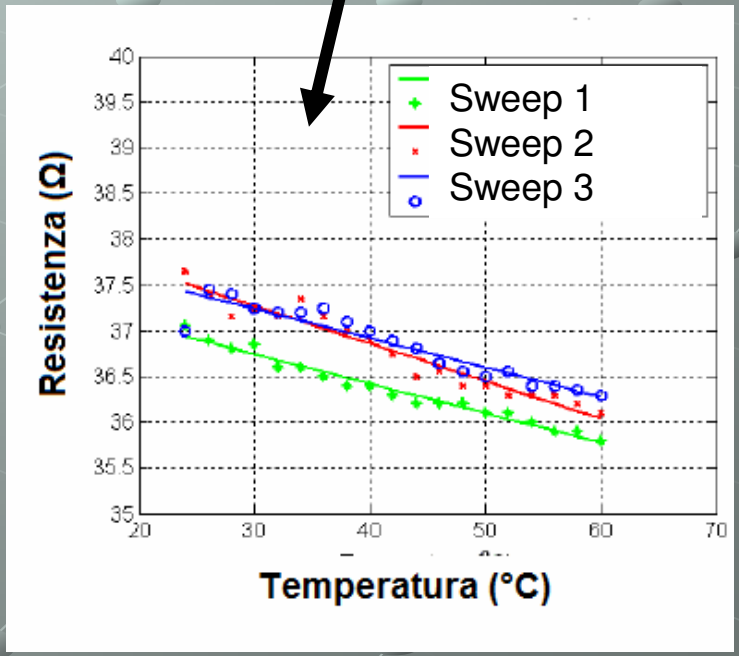


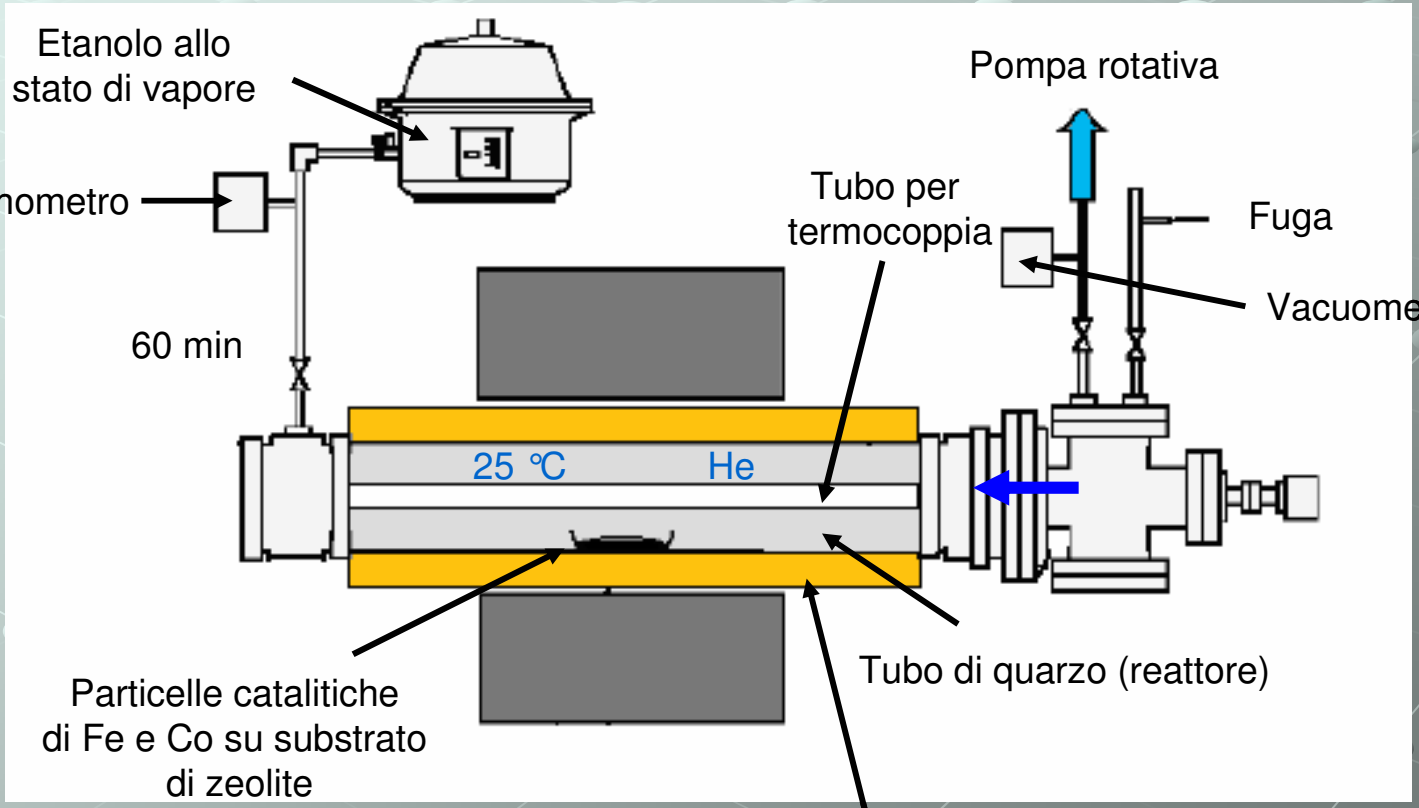
# SENSORE DI TEMPERATURA A CNT di FUNG ET AL.



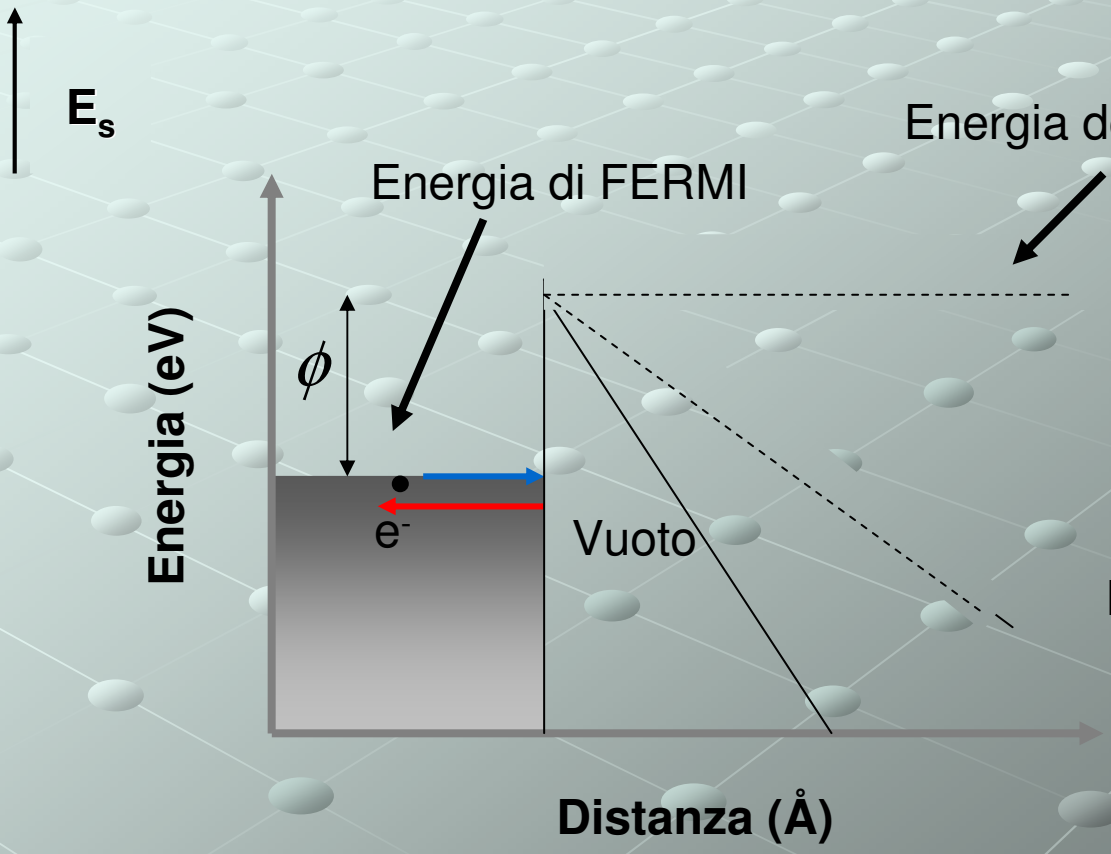

**TCR ~ -0.05 – -0.07 % $°C^{-1}$**



# DEPOSIZIONE CHIMICA DA VAPORE CATALITICA AD ALCOOL (produzione in larga scala di MWNT)



# EMISSIONE DI CAMPO

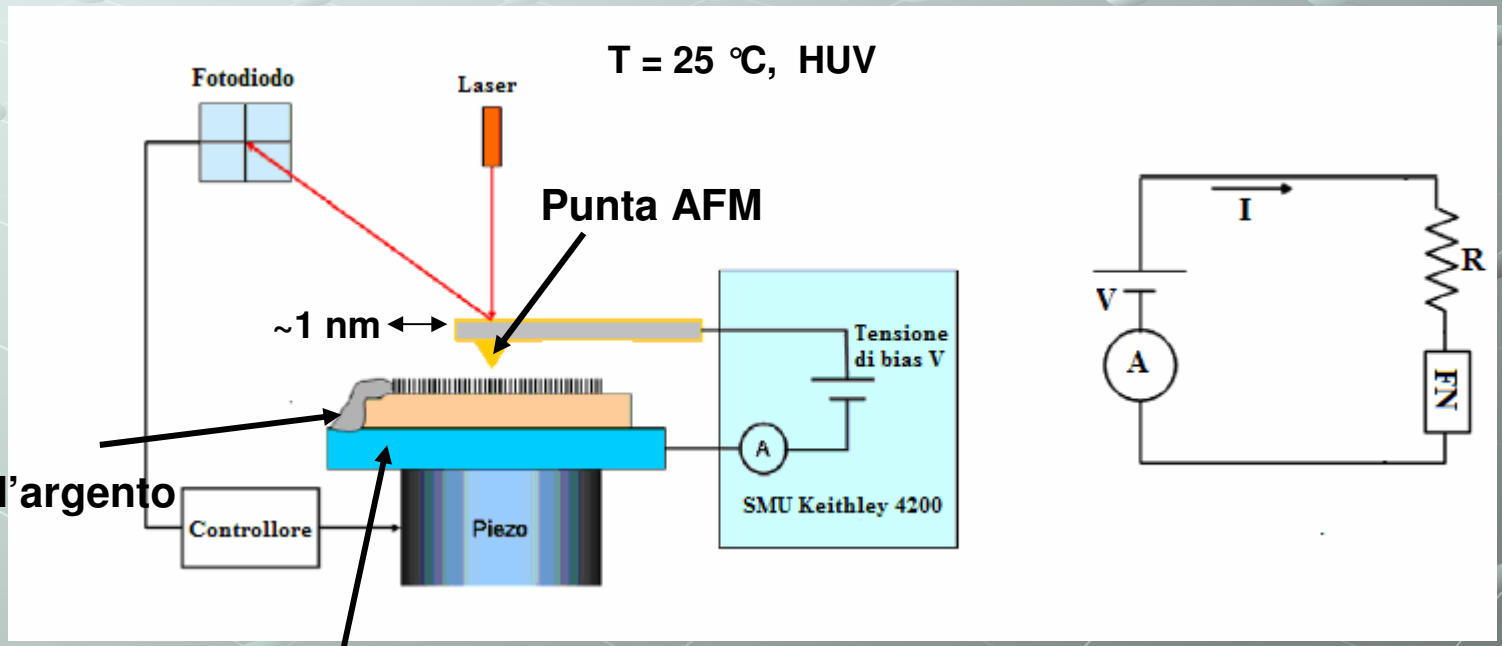



$$I = S\, a \frac{E_s^{\,2}}{\phi} e^{\left(-b\frac{\phi^{\frac{3}{2}}}{E_s}\right)}$$

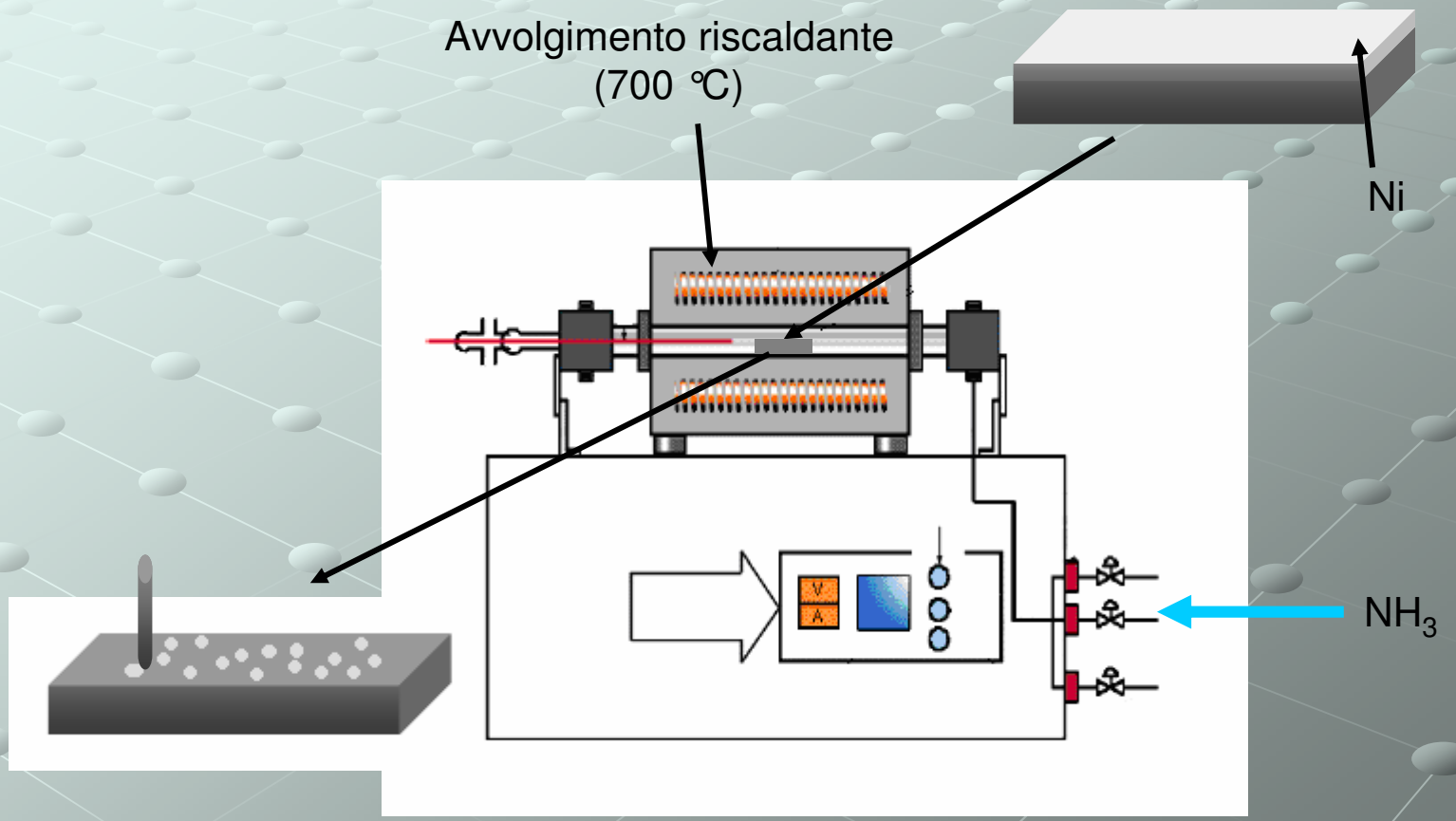
Modello di Fowler-Nordheim

# EMISSIONE DI CAMPO DA MWNT PARZIALMENTE ALLINEATI

## APPARATO DI MISURA DELLA FE



# CVD TERMICA



# EMISSIONE DI CAMPO DA MWNT PARZIALMENTE ALLINEATI

## CARATTERISTICA I-V