

# Nanopackaging: Nanotechnologies & Electronics Packaging

## Part B CNTs (1)

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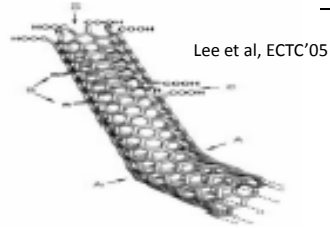


## Carbon Nanotubes (CNTs)

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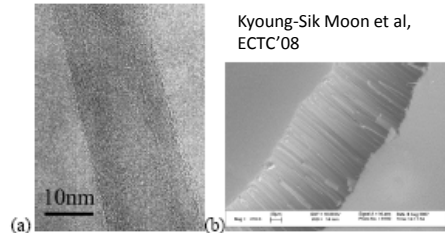
- General properties
- Preparation
- Mechanical
- Electrical
  - Shielding
  - Solder
  - Interconnects
- Thermal
- Miscellaneous applications

# Carbon Nanotubes (CNTs)



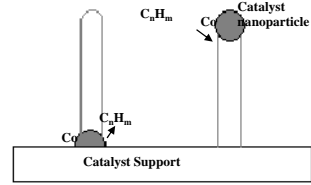
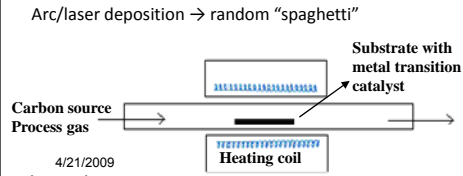
Lee et al, ECTC'05

Figure 1. Acid-modified surface structure of CNT



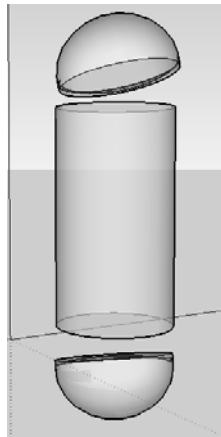
Kyoung-Sik Moon et al, ECTC'08

Figure 1. (a) TEM and (b) SEM images of aligned MWCNTs used.

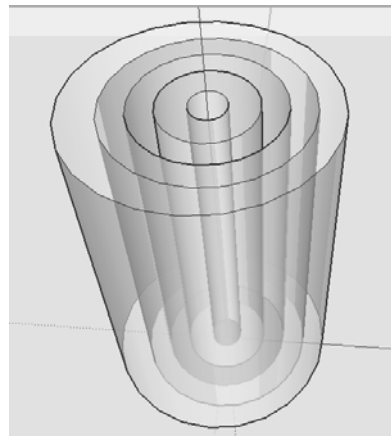


High T CVD V-L-S process: vertical growth, uniform lengths

# CNTs (Kunduru et al \*)

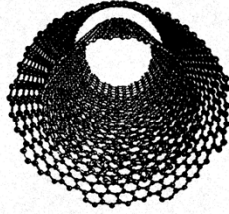


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MULTI WALLED CARBON NANOTUBES



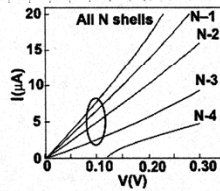
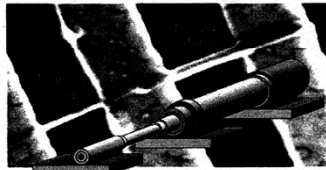
SWNT Single-walled nanotube  
MWNT Multi-walled nanotube

Each "shell" can have different indices, bandgaps, etc. Composite properties complicated.

Typically, outer shell conducts most current.

Contacts usually to outer shell

Figure 5.13. Illustration of a nested nanotube in which one tube is inside the another.



First 4 tube shells "coupled"

Fifth shell not coupled (> 0.1 V activation)

Figure 8<sup>34</sup> - Thinned MWNT, layers removed, along with an I-V plot after removal of each shell

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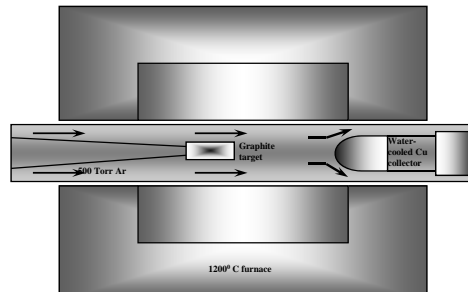
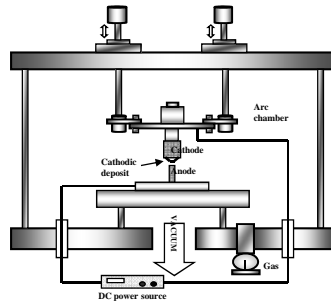
Table 3.1  
Physical Properties of Carbon Nanotubes

| Parameter                            | Value and units  | Observations   |
|--------------------------------------|--|--|
| Length of the unit vector            | $a = \sqrt{3}a_{C-C} = 2.49 \text{ \AA}$   | $a_{C-C} = 1.44 \text{ \AA}$ is the carbon bond length   |
| Current density                      | $> 10^9 \text{ A/cm}^2$  | -1000 times larger than the current density in copper  |
| Thermal conductivity                 | 6600 W/mK  | - Measured in MWCNTs<br>More thermally conductive than most crystals   |
| Young modulus                        | 1 Tpa  | Many orders of magnitude stronger than the steel   |
| Mobility                             | 10,000-50,000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  | Simulations indicate mobilities beyond 100,000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$                       |
| Mean free path (ballistic transport) | 300-700 nm semiconducting CNT<br>1000-3000 nm metallic CNT   | - Measured at room temperature<br>- At least three time larger than the best semiconducting heterostructures |
| Conductance in ballistic transport   | $G = 4e^2/h = 155 \mu\text{S}$ ;<br>$1/G = 6.5 \text{ k}\Omega$  |  |
| Luttinger parameter $g$              | 0.22   | The electrons are strongly correlated in CNTs  |
| Orbital magnetic moment              | 0.7 $\text{meV}\text{T}^{-1}$ ( $d = 2.6 \text{ nm}$ )<br>1.5 $\text{meV}\text{T}^{-1}$ ( $d = 5 \text{ nm}$ ) | The orbital magnetic moment depends on the tube diameter   |

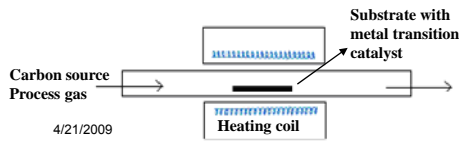
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# CNT Fabrication (Yadav et al)

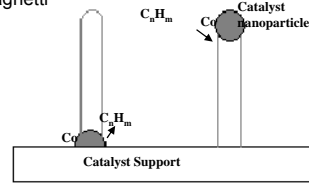


Arc/laser deposition → random "spaghetti"



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High T CVD V-L-S process: vertical growth, uniform lengths



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Figure 11 - Vapor-Liquid-Solid growth (VLS growth) mechanism of nanotubes

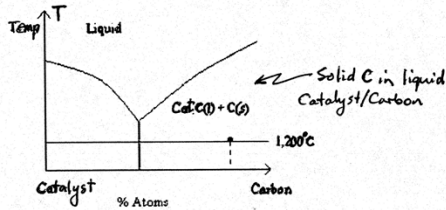
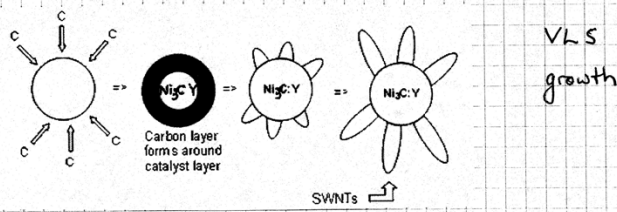


Figure 14 - Phase diagram, temperature chosen so the catalyst and carbon mixture is liquid and the pure carbon is solid.

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### 1.7.3 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is the easiest method, involving the layering a catalyst and then having a hydrocarbon gas react with it to grow nanotubes.

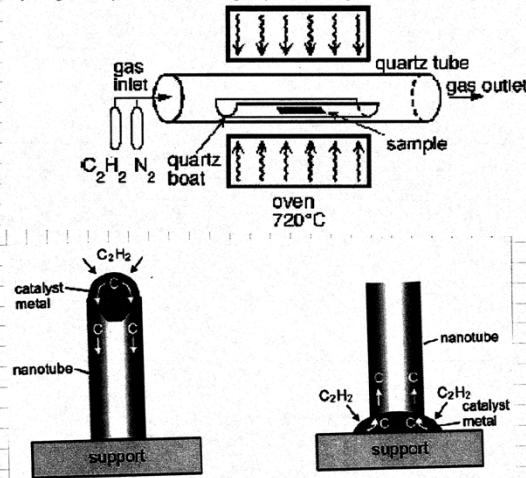


Figure 16<sup>43</sup> - Growth process during CVD production

Can also use methane (CH<sub>4</sub>) at 1100°C

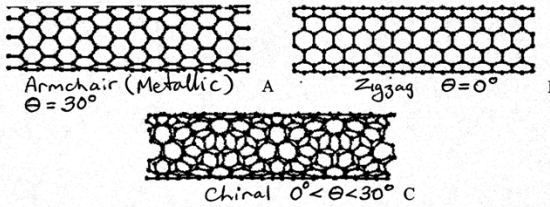
CVD →

- Cleanest CNTs
  - Open-ended CNTs (only method)
  - CNTs grow vertically on catalyst seeds (not tangled)
  - CVD is current IC fabrication technology
  - Growth similar to VLS, but slower
- ← Growth above or below catalyst

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### 3 classifications



A simple way to determine if a carbon nanotube is metallic or semiconducting is to look at the indices that describe it, (n, m). The nanotube will be metallic if  $n = m$  or  $n - m = 3i$ , where  $i$  is an integer. Otherwise, the tube is semiconducting. The  $n$  and  $m$  indices can also be used to check which of the three categories a nanotube fits in, zigzag, armchair, or Chiral. Figure 5 shows examples of all three.

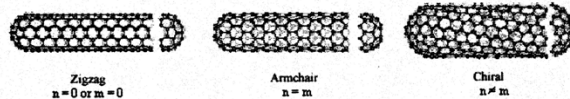


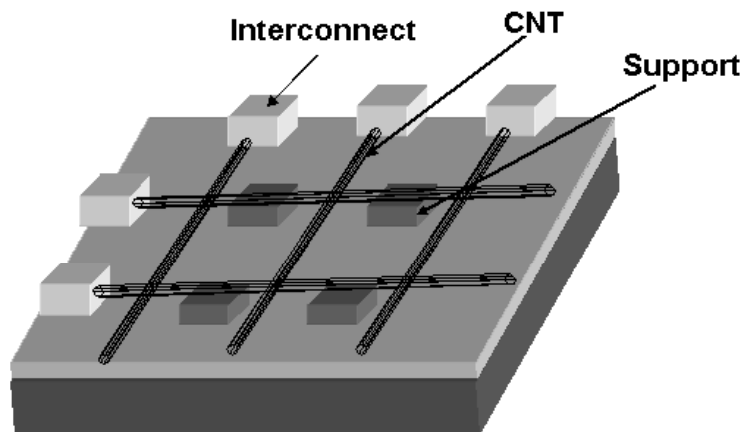
Figure 5<sup>11</sup> - Three types of Chirality.

The zigzag is characterized by its Zigzag shape, the armchair by its armchair shape, and the chiral by its twisted shape as highlighted. By combining figure 5 and the condition for type of conductor, armchair will always be metallic since  $n = m$ , while the others can be metallic or semiconductor. This is shown in figure 6.

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# Nantero CNT S-RAM (Kunduru et al \*) Rueckes et al (2000)



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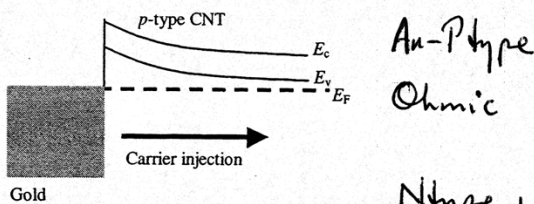


Figure 3.16 Ohmic contact between the p-type CNT and gold (After: [25]).

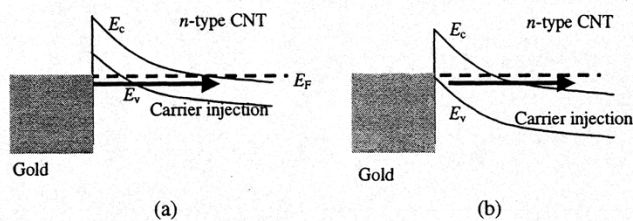


Figure 3.17 Contact between the n-type CNT and gold: (a) parasitic p-n junction, and (b) Schottky contact (After: [25]).

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# CNT Properties (Wikipedia)

CNT classifications:

|                 | Young's Modulus (Tpa)      | Tensile Strength (Gpa)    | Elongation at break (%) |
|-----------------|----------------------------|---------------------------|-------------------------|
| SWNT            | ~1 (1-5)                   | 13-53 <sup>E</sup>        | 16                      |
| Armchair        | 0.94 <sup>T</sup>          | 126.2 <sup>T</sup>        | 23.1                    |
| Zigzag          | 0.94 <sup>T</sup>          | 94.5 <sup>T</sup>         | 15.6-17.5               |
| Chiral          | 0.92 <sup>T</sup>          |                           |                         |
| MWNT            | 0.8-0.9 <sup>E</sup>       | 150                       |                         |
| Stainless steel | ~0.2                       | ~0.65-1.0                 | 15-50                   |
| Kevlar          | ~0.15 (0.25 <sup>T</sup> ) | ~3.5 (29.6 <sup>T</sup> ) | ~2                      |

Single wall SWNT  
Multi-wall MWNT

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Armchair  
Zigzag  
Chiral

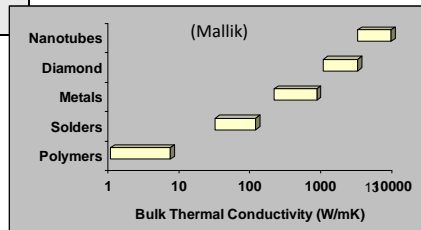
Metallic  
Semiconducting

SWNTs: typ. ½ metallic, ½ semicond  
Grow at ~ 900°C

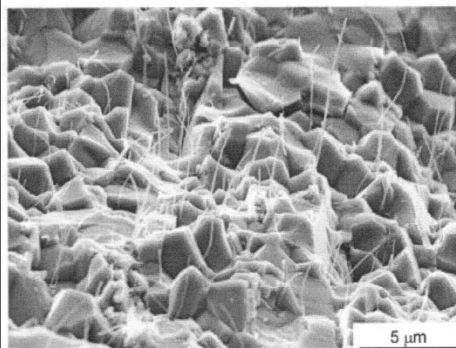
MWNTs: Metallic  
Grow at ~ 700°C (→365°C)

<sup>T</sup>Theoretical <sup>E</sup> Experimental

CTE ~ 0  
Electrical (Metallic CNT):  
 $I_{\max \text{ CNT}} > 1000 \times I_{\max \text{ Ag/Cu}}$   
 $\rho_{\text{CNT}} \sim 70 \times \rho_{\text{Si}}$   
CNT "ropes"  $10^{-4} \Omega \cdot \text{cm}$



# Mechanical Effects (Yamamoto, Nanotechweb.org)



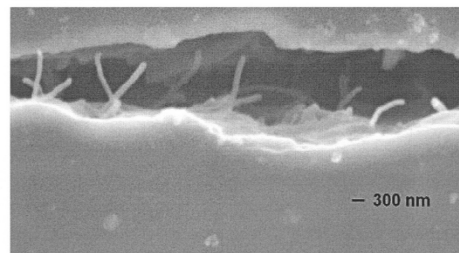
Fracture surface of MWCNT/alumina composite

0.9 vol % acid-etched CNTs:  
+27% bending strength  
+25% fracture toughness

Acid etch:

- Aids dispersion
- Increased interfacial friction
- Better than smooth CNTs

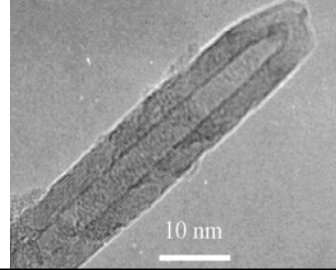
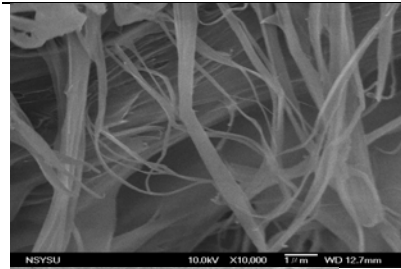
CRACK BRIDGING



SEM image of a fatigue crack being bridged by carbon nanotube fibres. (Image credit: Rensselaer Polytechnic Institute)

# EMC Shielding

## MWCNTs (Cheng et al)



CNTs in LCP

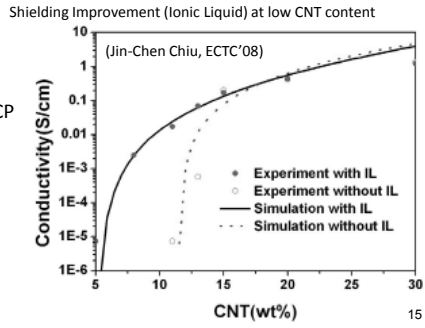
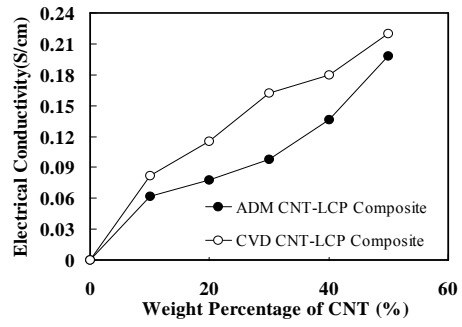


Figure 7 Conductivity of the MWCNT/PI composite at various weight percentage of MWCNT

# CNT Interconnect

(Naeemi, Huang, & Meindl, ECTC 2007)

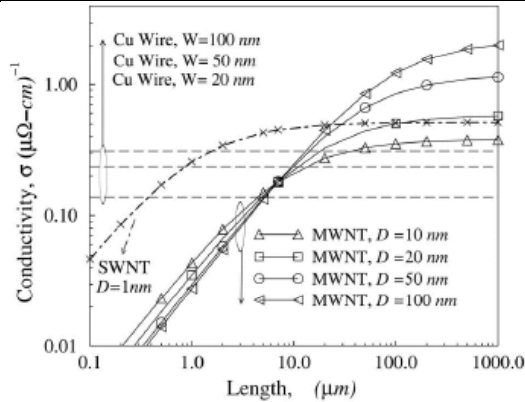


Figure 3: Conductivity of MWCNs with various diameters and bundles of densely packed SWCNs versus length. SWCNs are assumed to be 1nm in diameter and have random chiralities and a  $1\mu\text{m}$  mean free path.



# CNT Interconnect

(Banerjee, Li, Srivastava NANO 2008)

TABLE I. Comparison of properties among Cu, SWCNT, and MWCNT.

|                                   | Cu               | SWCNT                | MWCNT         |
|-----------------------------------|------------------|----------------------|---------------|
| Max. current density ( $A/cm^2$ ) | $<1 \times 10^7$ | $>1 \times 10^8$ [5] |               |
| Thermal conductivity ( $W/mK$ )   | 385              | 5800 [6]             | 3000 [7]      |
| Mean free path (nm) @ 300K        | 40               | $>1000$ [8]          | $>25000$ [9]* |

\* MFP of MWCNTs depends on their diameters. The value shown here is for the MWCNT with outmost shell diameter of 100 nm.

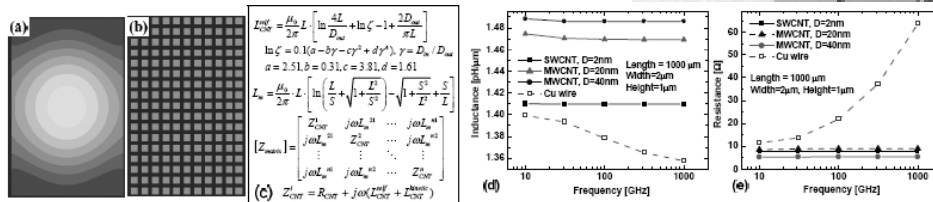
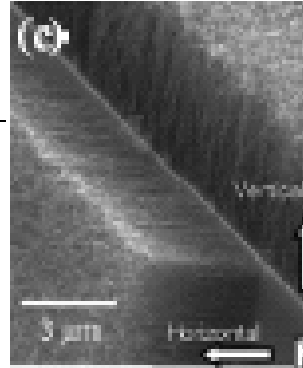
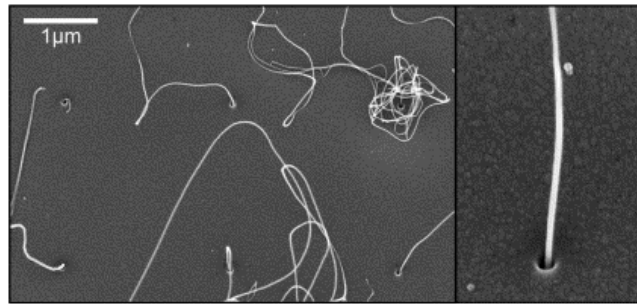
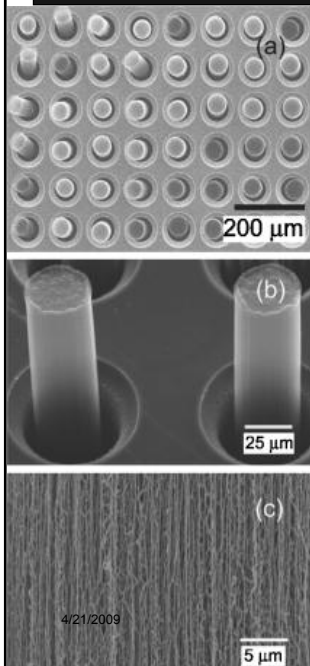


Fig. 10. (a) Current density distribution at 100 GHz of (a) single solid  $500 \text{ nm} \times 320 \text{ nm}$  cross-section interconnect, and (b) discrete conductor (each  $20 \text{ nm}$  square cross-section,  $10 \mu\text{m}$  interval) using electromagnetic field solver Maxwell [33]. Both of them have identical "equivalent conductivity", and identical current density is applied. Color coding in the two cases is identical. (c) Equations of inductance model.  $L_{Cnr}^{self}$  and  $L_{mn}$  are magnetic self- and mutual- inductance of each CNT.  $S$  is the distance between CNTs,  $Z_{mut, nr}$  is the impedance matrix of CNT bundle. Effective total (d) inductance, and (e) resistance of SWCNT and MWCNT bundles, and Cu interconnects as a function of frequency for the same dimension.

# CNTs in TSVs

← Xu et al, Appl Phys Lett (2007)

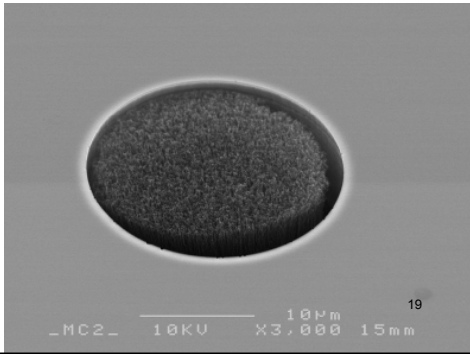
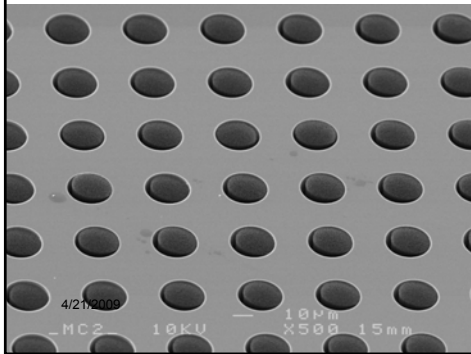
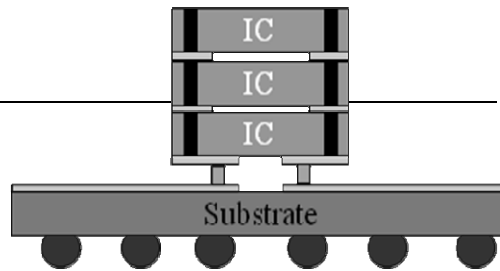


15nm MWNTs in 35nm vias  
Graham et al, Diamond & Related materials (2004)

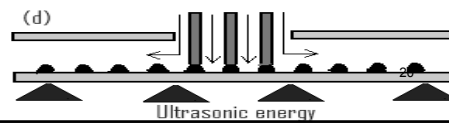
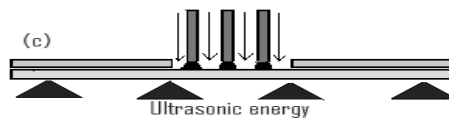
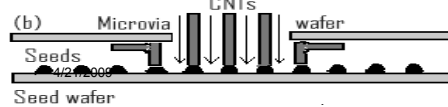
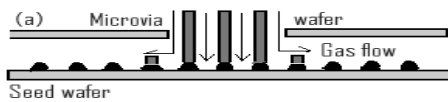
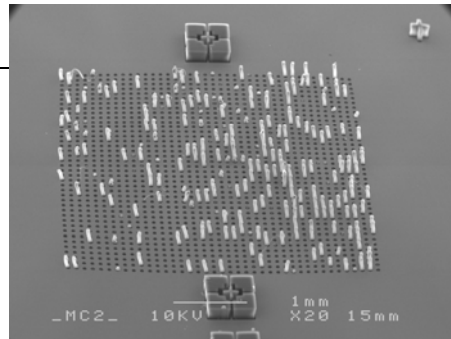
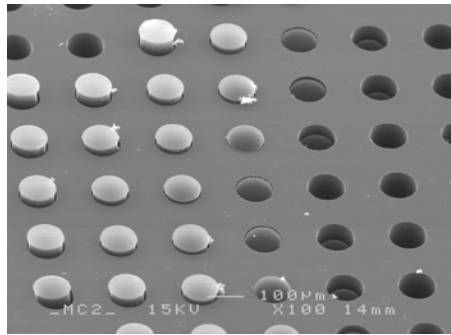
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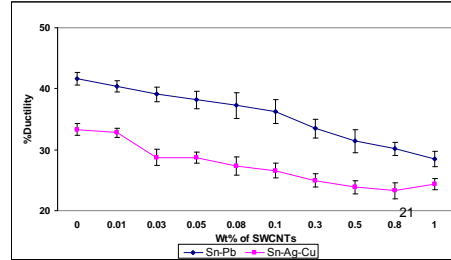
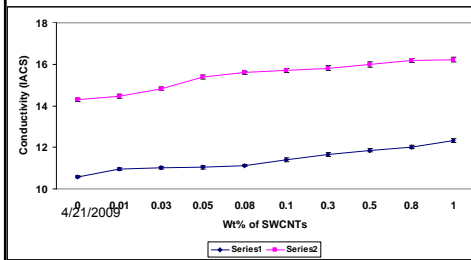
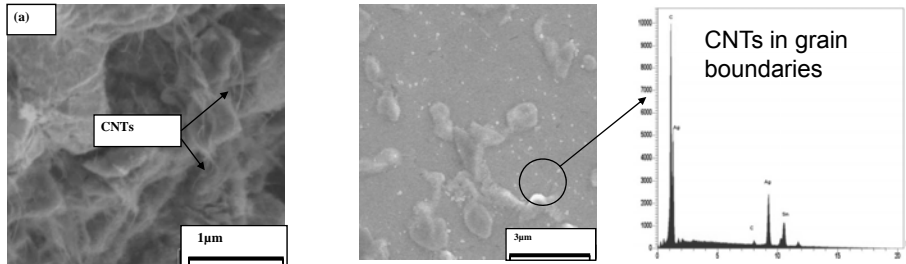
# 3D CNT TSVs (proposal)



# 3D CNT TSVs (proposal continued)

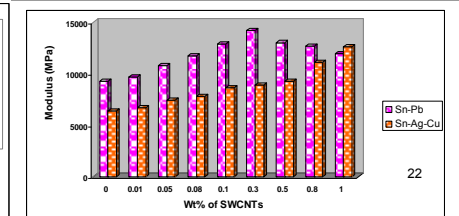
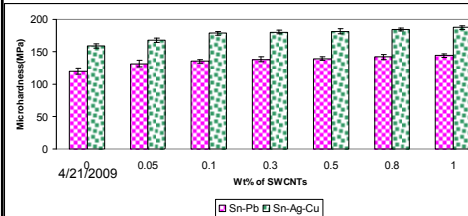
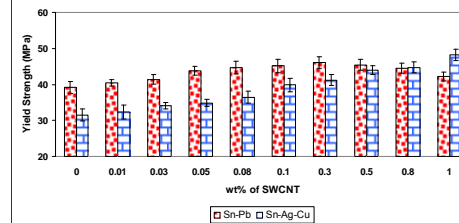
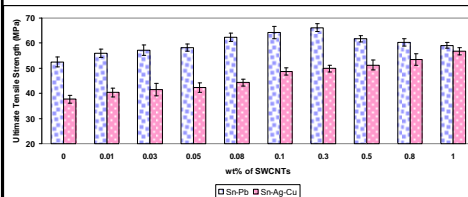
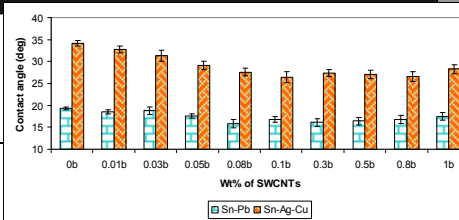


## SWCNT Effects on 63Sn-37Pb & Sn-3.8Ag-0.7Cu Solders (Kumar et al)



## SWCNT Effects on 63Sn-37Pb & Sn-3.8Ag-0.7Cu Solders (Kumar et al)

(Kumar et al)



# Ultimate tensile strength, etc [Kumar/Kripesh/Tay ECTC'06]

Table 2. Mechanical properties of the composite solders doped with nanotubes and nano particles.

| Type of Additive | SWCNT           |                |           | Nickel Nano Particles |                |           | Nano Molybdenum Particles |                |           |
|------------------|-----------------|----------------|-----------|-----------------------|----------------|-----------|---------------------------|----------------|-----------|
|                  | Wt% of Additive | Hardness (MPa) | UTS (MPa) | Ductility             | Hardness (MPa) | UTS (MPa) | Ductility                 | Hardness (MPa) | UTS (MPa) |
| 0                | 158.9           | 37.72          | 33.32     | 158.9                 | 37.72          | 33.32     | 158.9                     | 37.72          | 33.32     |
| 0.05             | 167.7           | 42.33          | 28.73     | 159.9                 | 38.65          | 33.12     | 162.8                     | 40.44          | 31.47     |
| 0.1              | 178.5           | 48.65          | 26.57     | 160.8                 | 40.56          | 32.18     | 165.7                     | 43.81          | 29.13     |
| 0.5              | 181.4           | 51.23          | 23.84     | 161.8                 | 41.87          | 33.18     | 169.7                     | 46.71          | 27.34     |
| 1                | 187.3           | 56.74*         | 24.36     | 165.7                 | 43.35          | 30.28     | 180.4                     | 51.33          | 24.35     |
| 2                | -----           | -----          | -----     | 168.7                 | 45.29          | 29.17     | 189.3                     | 54.73          | 23.26     |
| 2.3              | -----           | -----          | -----     | -----                 | -----          | -----     | 193.2                     | 58.37          | 22.69     |
| 2.5              | -----           | -----          | -----     | -----                 | -----          | -----     | 210.9                     | 61.46          | 24.31     |
| 2.8              | -----           | -----          | -----     | -----                 | -----          | -----     | 214.8                     | 64.51*         | 21.18     |
| 3                | -----           | -----          | -----     | 174.6                 | 47.91          | 27.53     | 219.7                     | 59.48          | 22.38     |
| 3.5              | -----           | -----          | -----     | 179.5                 | 51.07*         | 26.18     | 226.5                     | 56.39          | 19.71     |
| 3.8              | -----           | -----          | -----     | 185.4                 | 48.24          | 25.14     | -----                     | -----          | -----     |
| 4/21/2009<br>4   | -----           | -----          | -----     | 189.3                 | 45.29          | 23.22     | 234.4                     | 54.14          | 19.68     |

\* Indicates the maximum UTS values corresponding to the critical wt% of the reinforcement.

# Electromigration

(Yang Chai et al ECTC'08)

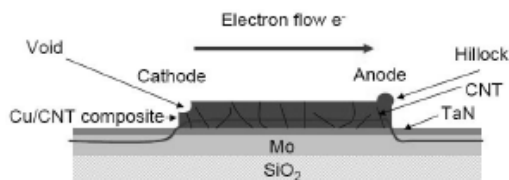


Figure 1: Schematic diagram of Blech-Kinsbron segment cross-section, showing shunting of current out of the bottom conductor into the top Cu/CNT stripe, depletion of the cathode, and mass accumulation at the anode.

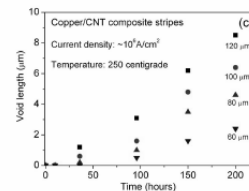
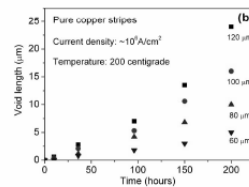
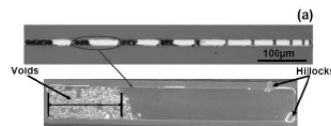


Figure 10: (a) Photograph of pure copper stripes with different lengths after EM testing, and SEM image of one of the segments; Plots of void growth length as a function of the stressing time for short (b) Cu and (c) Cu/CNT composite stripes.

4/21/2009 CNTs inhibit void growth

**Open-ended  
CNTs for  
electrical  
interconnect**  
[Zhu, Hess, Wong  
ECTC'06]

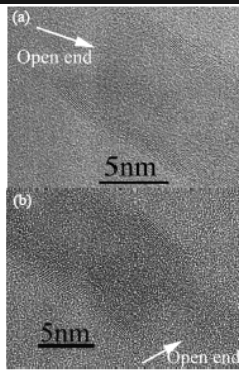


Figure 5. (a) and (b) HRTEM images of the two ends of an nanowire, showing that the two ends are open.

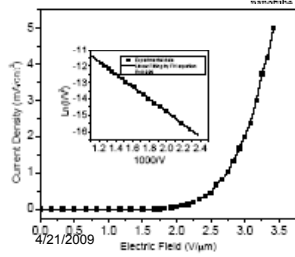
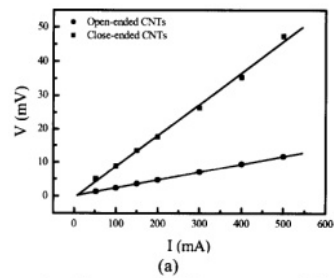
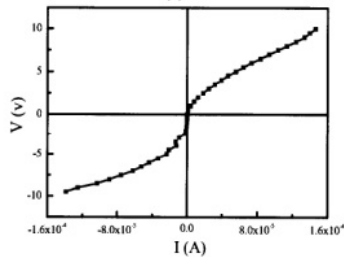


Figure 8. Field emission measurements of CNT films in (a) at room temperature.



(a)



(b)

Figure 6. I-V curves of (a) the open- and close-ended CNT films transferred by an ultra highly conductive adhesive and (b) open-ended CNT film transferred by a high resistivity conductive adhesive.