Control of the diameter and chiral angle distributions during production of single-wall carbon nanotubes

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Many applications of single wall carbon nanotubes (SWCNT), especially in microelectronics, will benefit from use of certain \((n,m)\) nanotube types (metallic, small gap semiconductor, etc.) Especially fascinating is the possibility of quantum conductors that require metallic armchair nanotubes. However, as produced SWCNT samples are polydisperse, with many \((n,m)\) types present and typical ~1:2 metal / semiconductor ratio.

Nanotube nucleation models predict that armchair nuclei are energetically preferential due to formation of partial triple bonds along the armchair edge. However, nuclei can not reach any meaningful thermal equilibrium in a rapidly expanding and cooling plume of carbon clusters, leading to polydispersity. In the present work, SWCNTs were produced by a pulsed laser vaporization (PLV) technique. The carbon vapor plume cooling rate was either increased by change in the oven temperature (expansion into colder gas), or decreased via “warm-up” with a laser pulse at the moment of nucleation. The effect of oven temperature and “warm-up” on nanotube type population was studied via photoluminescence, UV-Vis-NIR absorption and Raman spectroscopy.

It was found that reduced temperatures leads to smaller average diameters, progressively narrower diameter distributions, and some preference toward armchair structures. “Warm-up” shifts nanotube population towards arm-chair structures as well, but the effect is small. Possible improvement of the “warm-up” approach to produce armchair SWCNTs will be discussed. These results demonstrate that PLV production technique can provide at least partial control over the nanotube \((n,m)\) population. In addition, these results have implications for the understanding the nanotube nucleation mechanism in the laser oven.
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Production of armchair metallic nanotubes
  Why are armchair nanotubes interesting?
  Is it possible to make them?
  Two approaches to affect the cooling rate of SWCNT nuclei
  What about sample analysis?
Walking my dogs, Saturday September 13th. Hello, Ike!
What are single-wall carbon nanotubes?

MOLECULAR PERFECTION & EXTREME PROPERTIES

• The strongest fiber possible
• Thermal conductivity of diamond, anisotropic
• The unique chemistry of sp$^2$ carbon
• The scale and perfection of DNA
• Selectable electrical properties: Metallics and Semiconductors
• The ultimate engineering material
• SWCNT behaves as a molecule and as a macro object at the same time!
The graphene sheet can be rolled in many possible ways:

- Armchair, $\alpha = 30^\circ$
- Zig-zag, $\alpha = 0^\circ$
- Intermediate, $0^\circ < \alpha < 30^\circ$

Electrical properties depend on this.
Rolling Graphite: n,m Vectors

- Of the 864 distinct types between 0.7 and 2.8 nm diameter,
- ~ 1/3rd are semi-metals
- ~ 2/3rd direct band-gap semiconductors
- Only 16 are armchair metals!
- Even smaller fraction for typical PLV-produced SWNT in 0.9 – 1.6 nm diameter range
Nanotubes in microelectronic devices

Room-temperature transistor based on a single carbon nanotube

An Integrated Logic Circuit Assembled on a Single Carbon Nanotube

More recent and realistic proposals: Can we use metallic SWNT as interconnects on microchips?
Metallic nanotubes

What are they good for?

• Interconnects on microchips – certainly an excellent idea.

• Measurements on individual metallic SWNT on Si wafers with patterned metal contacts

• Single tubes can pass 20 µA for hours
• Equivalent to roughly a billion amps per square centimeter!

• Conductivity measured twice that of copper
• Ballistic conduction at low fields with mean free path of 1.4 microns
• Similar results reported by many

• Common metals give away their electrons too easily at these conditions and oxidize away. sp² electrons are much more stable!

Armchair metallic nanotubes

But nanotubes have final length
Can we make a good electrical conductor out of discontinued wires?
Answer – resonant quantum tunneling

An interesting feature of this junction is the sensitive dependence of conductance on the contact length, \( l \). Figure 2 shows the conductance values for armchair-armchair and

![Graphs](image)

FIG. 1. (a) A two-terminal nanotube junction can be formed by bringing two tubes’ ends together in parallel and pointing opposite directions (\( l \) is the contact length). (b) The transmission coefficient \( T \) of the two armchair tube [(10,10)-(10,10)] junction as a function of energy \( E \) for \( l = 64 \) Å. Interference of electron waves yields resonances in transport. (c) Current-voltage characteristics of the (10,10)-(10,10) junction for \( l = 46 \) Å.

Armchair metallic nanotubes

- Experimental evidence of resonant tunneling
- Indirect indication of conductivity by measuring lifetimes of photo-excited electrons
- Cooling mechanism is interaction with phonons – just like electrical resistivity
- Anomalously long life-times yield mean free path of 15 microns (10x single tubes)
- Based on bundles in ‘buckypapers’ – good local symmetry and clean, but still based on mixture of metals and semi-conductors
- Results imply 10 – 25x better conductivity than copper

So far all optimization was centered on increasing production rate and nanotube yield.

Can we optimize for the nanotube type?

Green – IR, 50ns delay to optimize ablation rate.
Nanotube nucleation occurs in the 100 $\mu$s – 1 ms time frame, from carbon clusters and catalyst vapor.

- Carbon has much lower vapor pressure than metal catalyst
- Carbon atoms condense first and form small graphene sheets that start closing into cages
- Without metal, cage closes into a fullerene ( ~40% yield, and 1-3% in typical nanotube sample)
- When metal atom lands on the edge, it satisfies dangling bonds and prevents cage from closing
- When cluster exceeds 500-600 carbon atoms, it’s shape is fixed kinetically, and the nanotube keeps on growing by adding incoming carbon clusters to the open end

Formation of the nanotube nuclei with fixed (n,m) happens on the time scale of 100 $\mu$s – 1 ms – very fast. Subsequent growth occurs on the few seconds scale

Interesting observation: armchair (n=m) nuclei are ~15% more stable energetically due to formation of triple bonds. However, equilibrium is not reached due to the very fast nature of the nucleation

$$\varepsilon_e \text{ zig-zag} > \varepsilon_e \text{ armchair}$$

Can we affect nanotube nucleation?

- Faster nucleation – expansion into a colder gas
- “Warm-up”: hit nanotube nuclei with more energy after the nucleation time, slow down cooling, and let them to nucleate longer.


Nanotube production at lowered temperature.

So, we decided to try 1100, 1000 and 900 °C temperatures. Everything else – the same: Co/Ni catalyst (1 at. % each). Argon buffer gas at 500 Torr pressure and 100 sccm flow rate. Green/IR ablation laser combination (2nd and 1st harmonics of Nd:YAG lasers) with 50 ns pulse delay, 1.6 J/cm² energy density each and 60 Hz repetition rate.
Preparing these samples was easy.
What needs to be done to understand how temperature influences SWCNT population?

Absorption spectra: too much overlapping of the spectral features
Discriminate semiconducting tubes with the help of photoluminescence.

- **Full PL maps** on J-Y Spex Fluorolog 3-211 equipped with an LN$_2$-cooled InGaAs NIR detector. 5 nm excitation step, 3 nm detection step, 5 nm slits.

- Only 12 - 14 semiconducting tubes.

- In order to measure peak amplitudes precisely, each peak is fitted with 2-d Lorentzian
Resulting chiral maps: semiconductors only
Metallic tubes: no PL makes similar analysis impossible.

On absorption spectra each metallic peak is a superposition of several possible tubes – impossible to deconvolute

Raman: 514 nm excitation is reasonably in tune with first peak. Will also excite large diameter semiconductors on $S_{33}$ transition

633 nm excitation is reasonably in tune with 2nd and 3rd peaks

RBM frequencies are much better known and reproducible.

Example: 1000 C sample
Raman spectra deconvolution

514 nm 1000°C

633 nm 1000°C

Excitation is off-resonance:
Use excitation profile and assume that linewidth and overtone tail scale with the transition energy RBM frequencies are known to shift due to bundling, etc. However it is possible to find an “ancor” tube ((9,6), (13,1) in this case) and determine the RBM frequencies of the other tubes.
The larger diameter tubes have chiral angles closest to arm-chair (30°)
Ec, is to a good approximation independent of tubulet radius (determined by 5 pentagons in a hemisphere).

Er = \varepsilon_r L/R, where \varepsilon_r is bending stiffness of a graphene sheet, L is length of the cylinder, and R is tubulet radius.

E_e = 2\pi R \varepsilon_e, where \varepsilon_e is energy of the open edge per unit length.

Minimization of the energy with respect to R for a fixed number of carbon atoms N yields:

R \sim \left( \frac{N \varepsilon_r}{\varepsilon_e} \right)^{1/3}.

Therefore, decrease in the edge energy \varepsilon_e will lead to increase in the diameter of a nanotube nucleus.

If \varepsilon_e armchair < \varepsilon_e zig-zag, nuclei with the edge closest to arm-chair structure will nucleate largest diameter nanotubes.
“Warm-up” approach: what should be the energy density and time delay?

Time delay: 500 μs. (decided rather arbitrarily)
Energy density:
Green energy: 1.6 J/cm²
-UV: avoid secondary ablation
-UV energy varied, looking at increase in C₂⁺ emission on top of black body continuum. Secondary ablation threshold ~0.1 J/cm² for 500 μs delay.
Oven temperature: 1000 °C. We need to bring SWCNT diameter within the reach of spectroscopy tools.

~180 K increase for ~ 100 μs
Nanotube population: is it enriched in armchair structures as a result?

Discriminate semiconducting tubes with the help of photoluminescence.

• Full PL maps on J-Y Spex Fluorolog 3-211 equipped with an LN$_2$-cooled InGaAs NIR detector. 5 nm excitation step, 3 nm detection step, 5 nm slits.

• Only 14 semiconducting tubes.

• Maps appear similar. In order to measure small differences, each peak is fitted with 2-d Lorentzian
PL data:

(9,7), (9,8), and (8,7) increase with warm-up - all have chiral angles >25°, close to armchair

(13,2), (12,4), and (10,5) decrease with warm-up - all have chiral angles <20°

No clear diameter dependence

Absorption data is consistent with this.
Chiral map.
Raman data:

(8,8), (10,7), and (9,6) increase with warm-up
-all have chiral angles >23°, close to armchair

(12,6), (11,5), (13,4) and (14,2) decrease with warm-up
-all have chiral angles <20°

(9,9) did not change

(15,0) and (13,1) increase with warm-up: smallest chiral angles

No clear diameter dependence

(12,0), (11,2) and (10,4) are not present on Raman spectra
Chiral map.
Conclusions

• Semiconducting nanotubes close to armchair structure increase

• Metallic nanotubes close to armchair structure increase

• 1 zig-zag metallic tube also increase

• The effect of “warm-up” on nanotube population is small, but definitely noticeable, considering that type population in PLV production is highly reproducible.

• Longer warm-up is needed. 5 ns pulse is only enough to raise temperature by ~180k for 100 µs at most.

• Long-pulse laser? UV Hg flash lamp? Intensity ramp?

• Optimization with respect to the time delay. Nanotube nucleation timeline is still unknown. 500 µs time delay used in this work is no more than an educated guess.