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

Pavel Nikolaev, ERC Inc. / NASA Johnson Space Center, Houston, TX

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

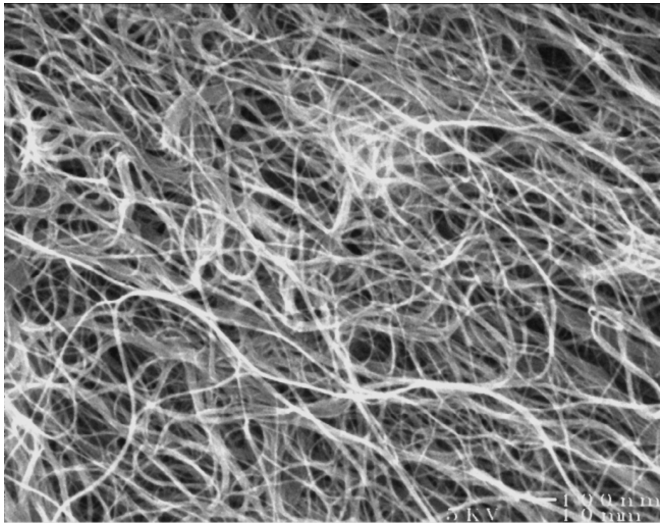
- Why are armchair nanotubes interesting?
- Is it possible to make them?
- Two approaches to affect the cooling rate of SWCNT nuclei
- What about sample analysis?

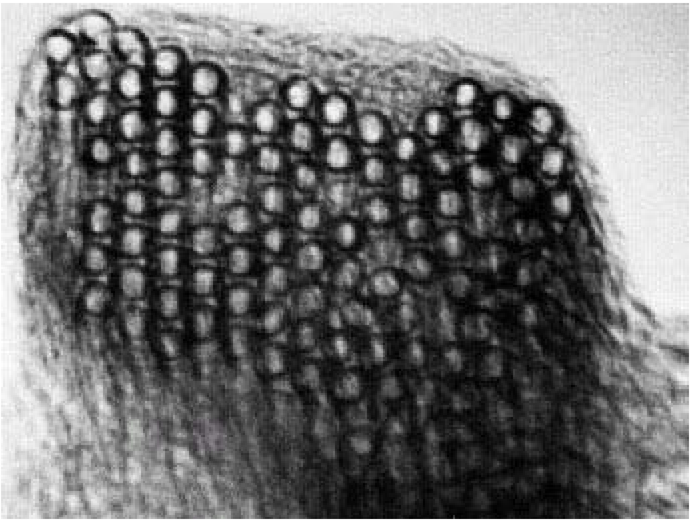
Walking my dogs, Saturday September 13th. Hello, Ike!

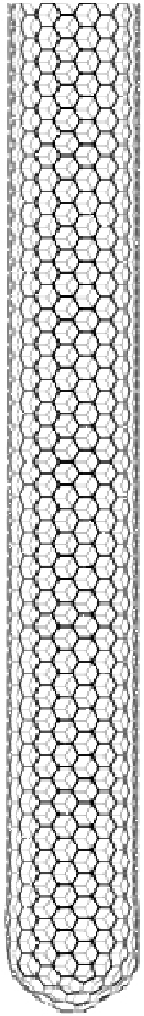
What are single-wall carbon nanotubes?

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!*





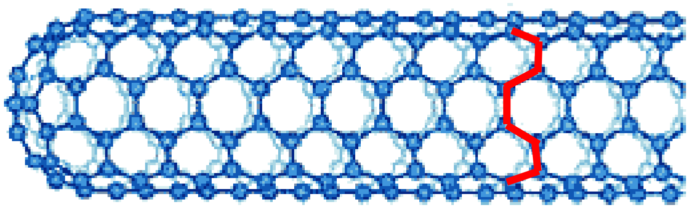


Let’s roll

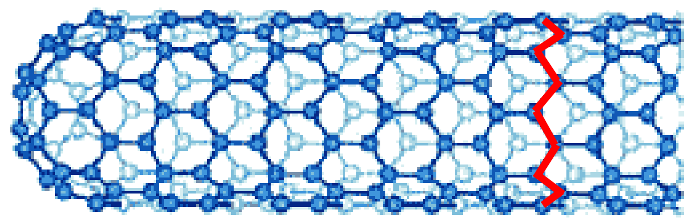
- The graphene sheet can be rolled in many possible ways

- Armchair, α = 30^{o}
- Zig-zag, α = 0^{o}
- Intermediate, 0^{o}<α<30^{o}

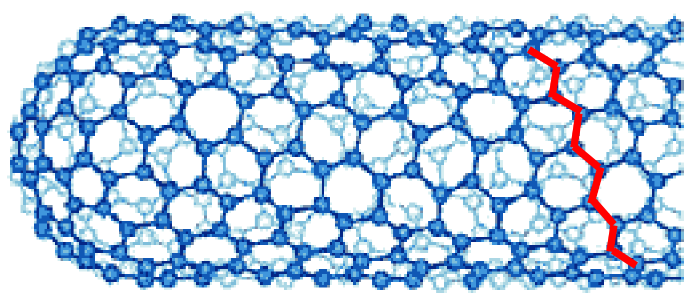
Electrical properties depend on this.



Armchair (α = 30°)



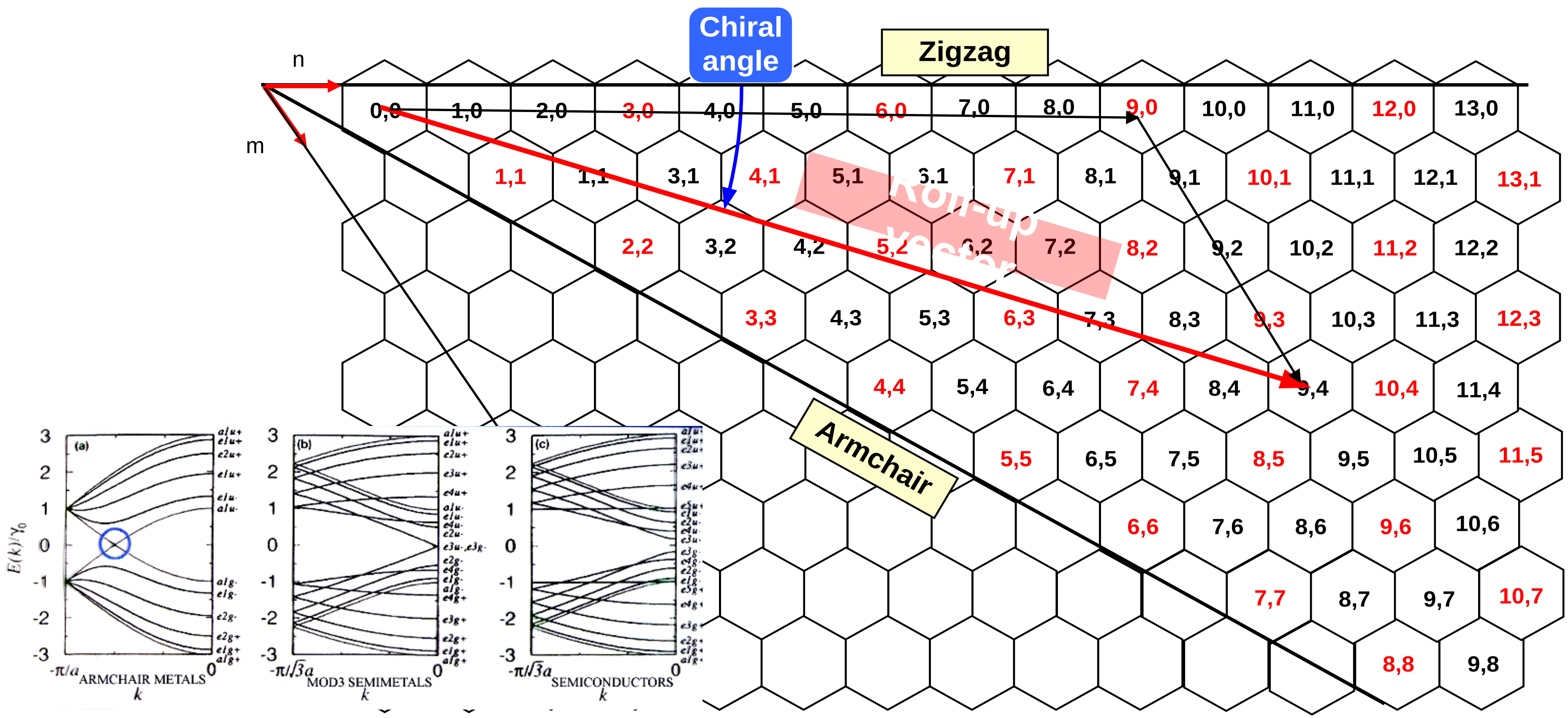
Zigzag (α = 0°)



Intermediate (0< α < 30°)

Rolling Graphite: n,m Vectors

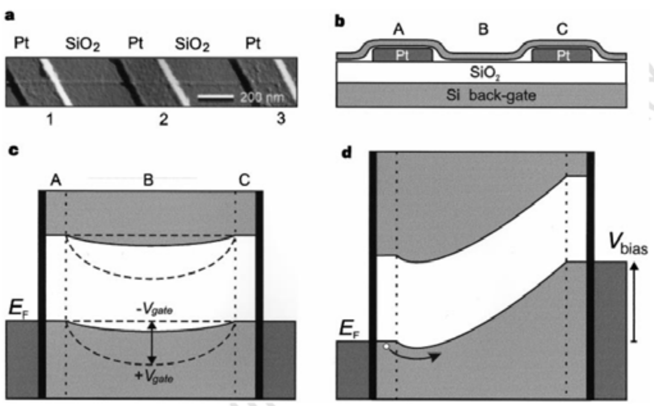
- **Of the 864 distinct types between 0.7 and 2.8 nm diameter,**
- **~ 1/3rd are semi-metals**
- **~ 2/3rd direct band-gap semiconductors**
- **Only 16 are armchair metals!**
- **Even smaller fraction for typical PLV-produced SWNT in 0.9 – 1.6 nm diameter range**



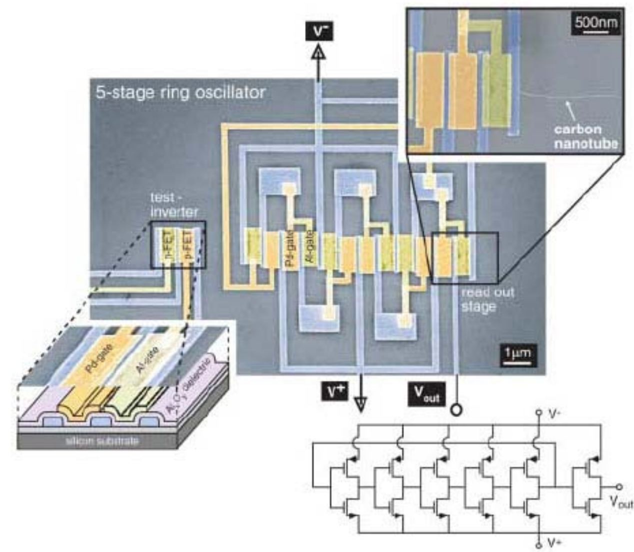
n=m mod3(n-m)=0 mod3(nim)=1 or 2

Nanotubes in microelectronic devices

1997 - 1998



Room-temperature transistor based on a single carbon nanotube
Sander J. Tans, Alwin R. M. Verschueren & Cees Dekker,
Nature vol. 393, 7 May 1998



2005-2006

An Integrated Logic Circuit Assembled on a Single Carbon Nanotube
Zhihong Chen, Joerg Appenzeller, Yu-Ming Lin, Jennifer Sippel-Oakley, Andrew G. Rinzler, Jinyao Tang, Shalom J. Wind, Paul M. Solomon, Phaedon Avouris,
Science vol. 311, 24 March 2006

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

Metallic nanotubes

What are they good for?

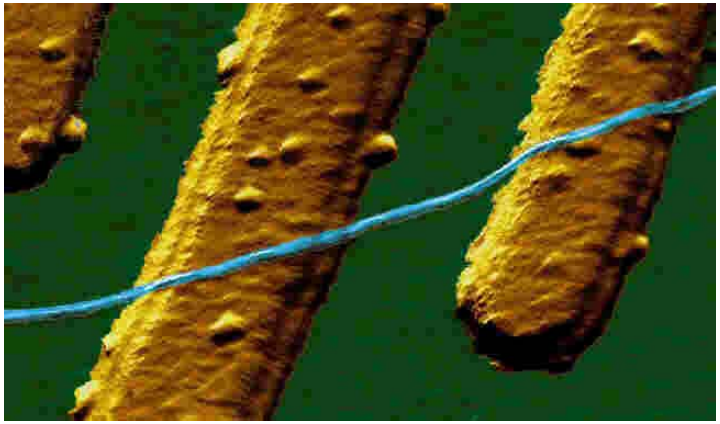
•Interconnects on microchips – certainly an excellent idea.

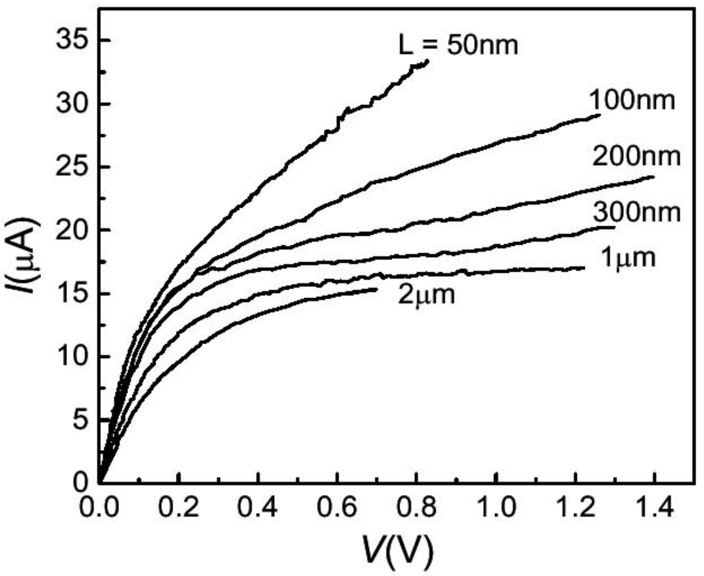
•Measurements on individual metallic SWNT on Si wafers with patterned metal contacts

•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. sp^2 electrons are much more stable!





Dekker, Smalley, *Nature*, **386**, 474-477 (1997). McEuen, et al, Phys.Rev.Lett.**84**, 6082 (2000)

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

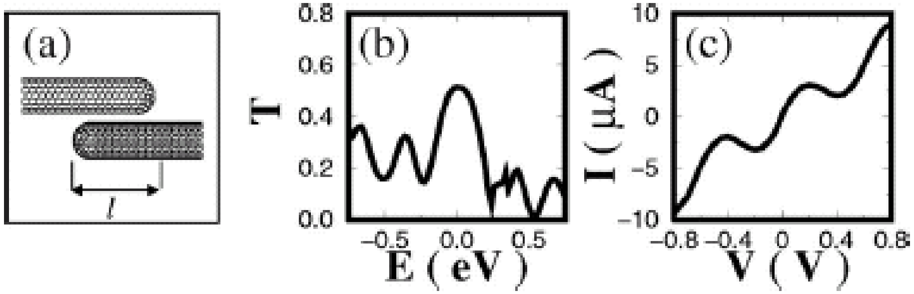
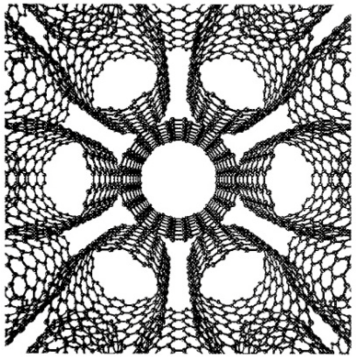


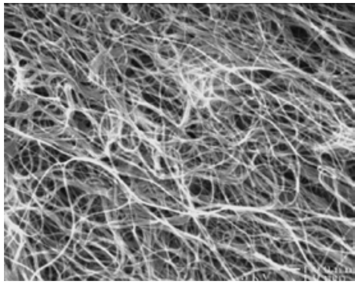
FIG. 1. (a) A two-terminal nanotube junction can be formed by bringing two tubes' ends together in parallel and pointing opposite directions (l is the contact length). (b) The transmission coefficient T of the two armchair tube [(10,10)-(10,10)] junction as a function of energy E for $l = 64$ Å. Interference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

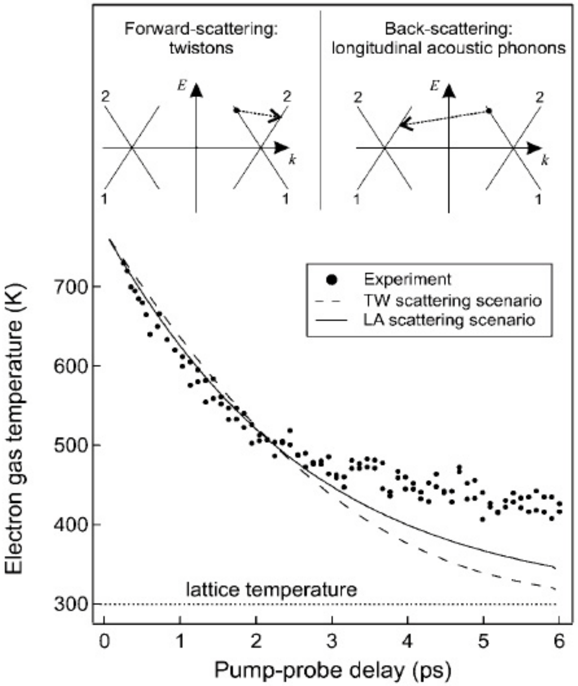
Alper Buldum and Jian Ping Lu, Phys. Rev. B 63, 161403 R (2001).

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

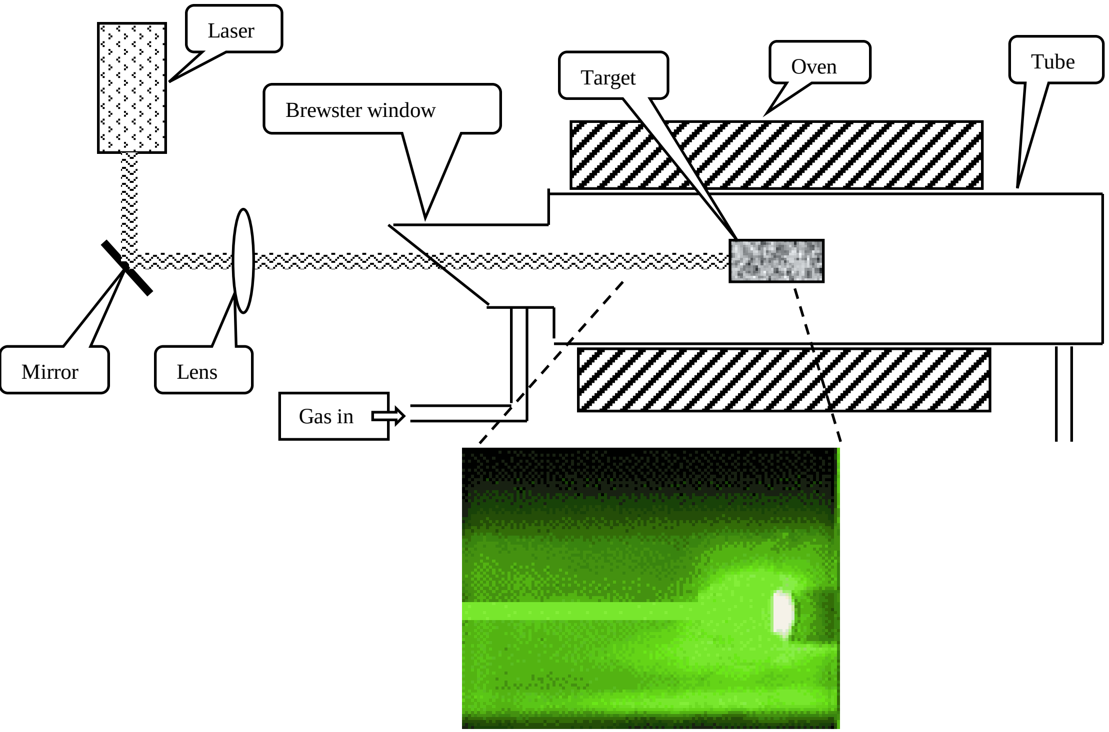


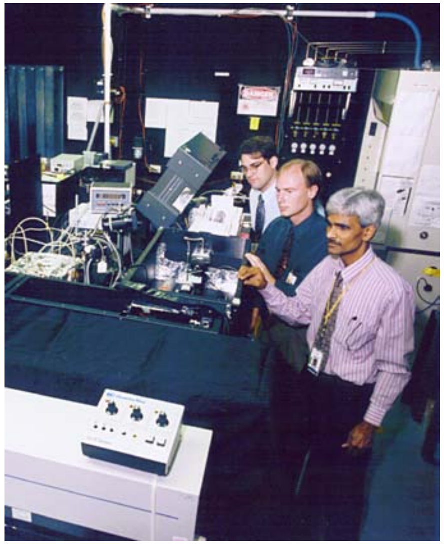


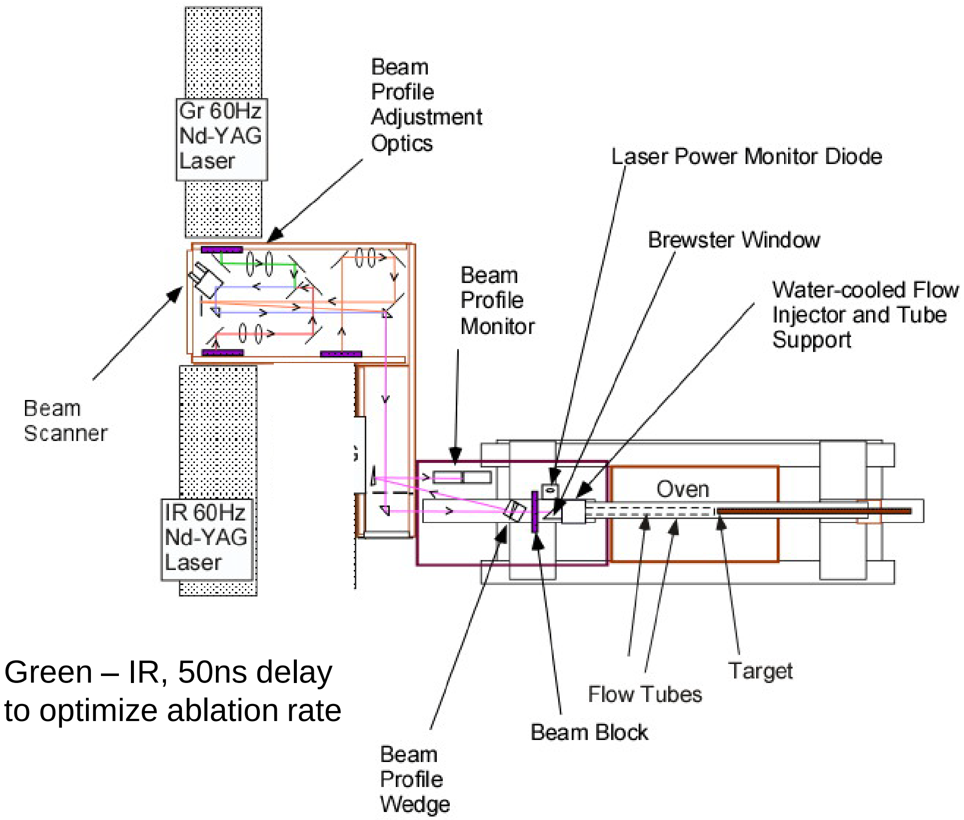


Source: Tobias Hertel, et al, *Phys. Rev. Lett*. 84(21) (**2000**) 5002

SWCNT production by PLV at Johnson Space Center





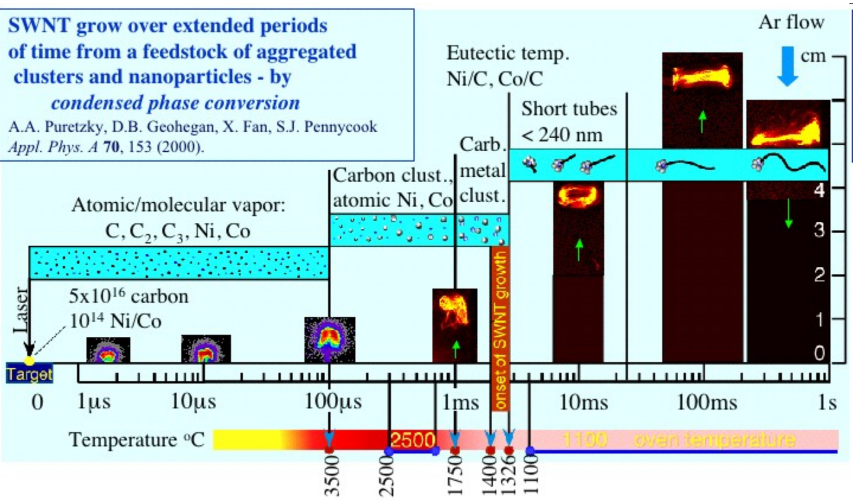


So far all optimization was centered on increasing production rate and nanotube yield

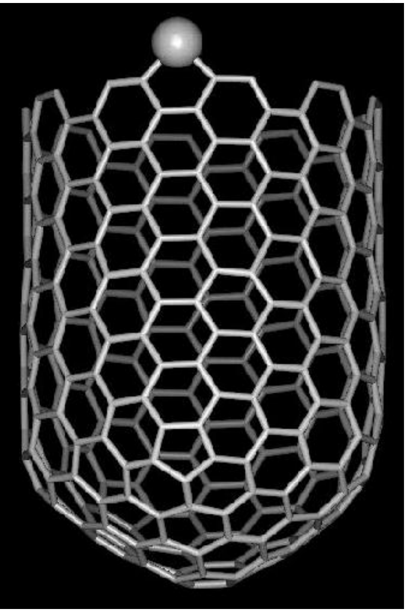
Can we optimize for the nanotube type?

Green – IR, 50ns delay to optimize ablation rate

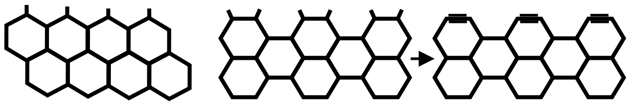
Nanotube nucleation in laser oven



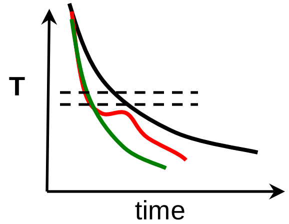
- •Nanotube nucleation occurs in the 100 μs – 1 ms time frame, from carbon clusters and catalyst vapor.
- •Carbon has much lower vapor pressure than metal catalyst
- •Carbon atoms condense first and form small graphene sheets that start closing into cages
- •Without metal, cage closes into a fullerene (~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 μs – 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



ε_e zig-zag > ε_e 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.**

A. Thess, R. Lee, P. Nikolaev, H. J. Dai, P. Petit, J. Robert, C. H. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer, and R. E. Smalley, *Science* 273, 483 **(1996)**.

Y. H. Lee, S. G. Kim, and D. Tománek, *Phys. Rev. Lett.* 78, 2393 (**1997**).

Nanotube production at lowered temperature.

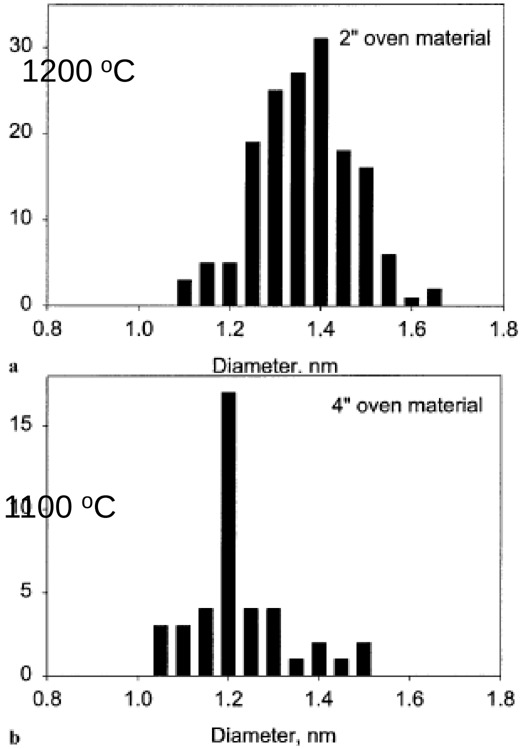


Fig. 5. **a** The diameter distribution of SWNT made in the 2" system (1200 °C). **b** The diameter distribution of SWNT made in the 4" system (1100 °C)

Co/Ni catalyst, 1200 and 1100 °C

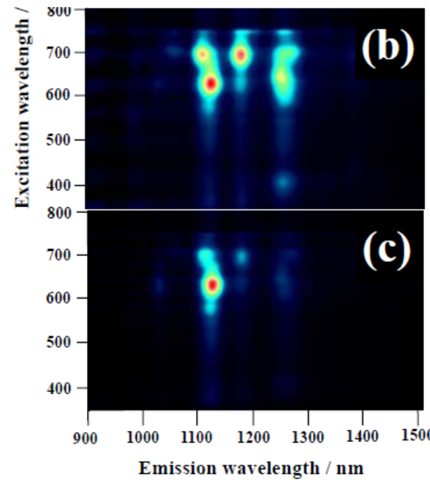
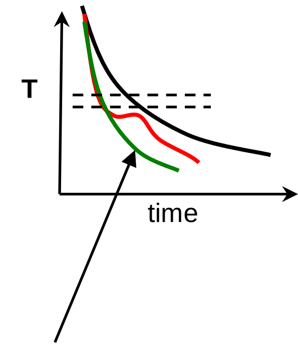


Fig. 4. (Color online) Photoluminescence mapping of dispersed SWNTs in sodium dodecyl benzenesulfate (SDBS) solution. (a) HiPco nanotubes. (b) SWNTs prepared in nitrogen atmosphere. (c) SWNTs prepared in Ar atmosphere.

Rh/Pd catalyst, 1150 °C
(vs. normal 1400 °C)



1.A. G. Rinzler, J. Liu, H. Dai, P. Nikolaev, C. B. Huffman, F. J. Rodriguez-Macias, P. J. Boul, A. H. Lu, D. Heymann, D. T. Colbert, R. S. Lee, J. E. Fischer, A. M. Rao, P. C. Eklund, and R. E. Smalley, *App. Phys. A* 67, 29 **(1998).**

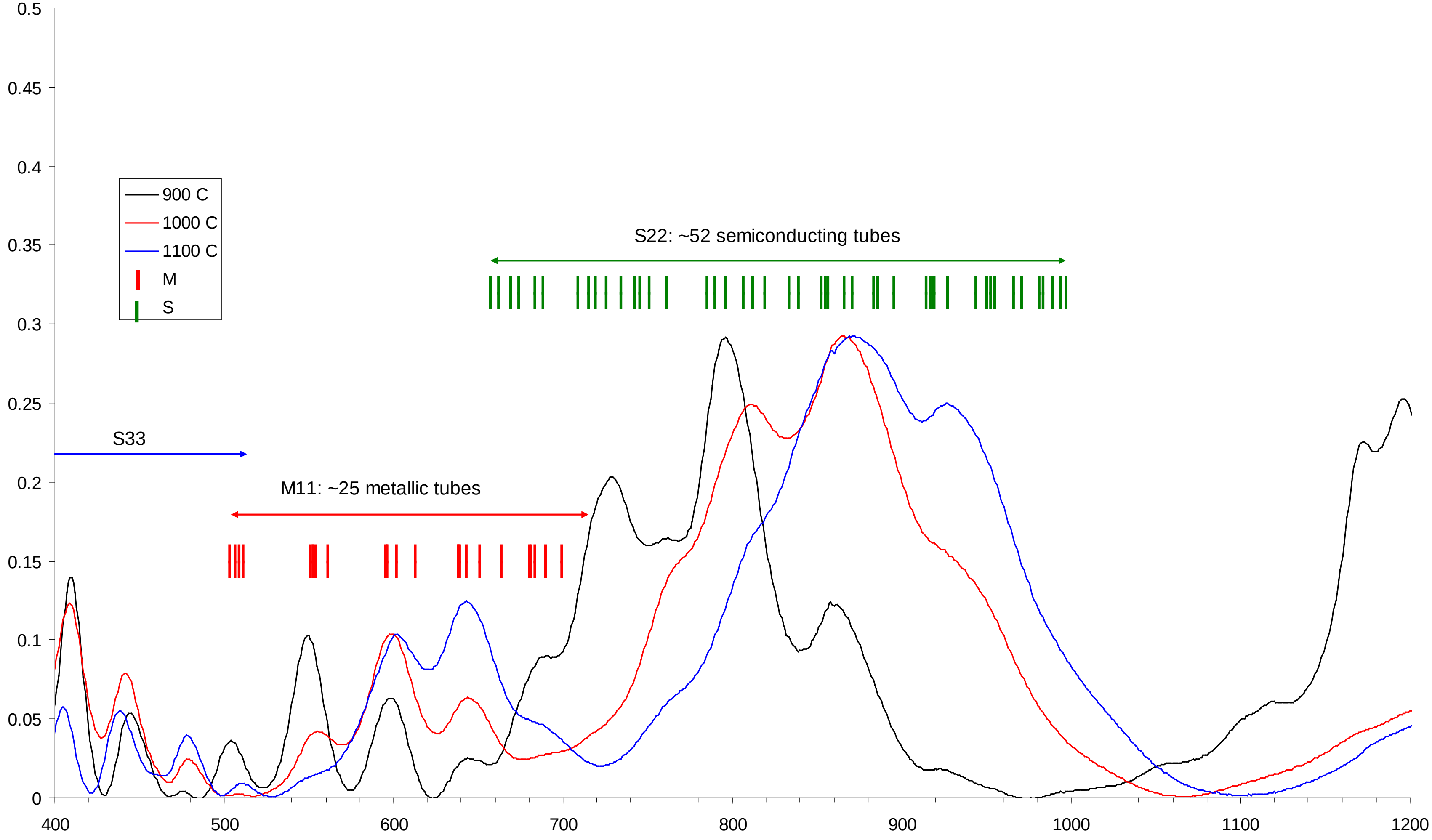
S. Suzuki, N. Asai, H. Kataura, and Y. Achiba, *Eur. Phys. J. D* 43, 143 **(2007).**

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/cm^2 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



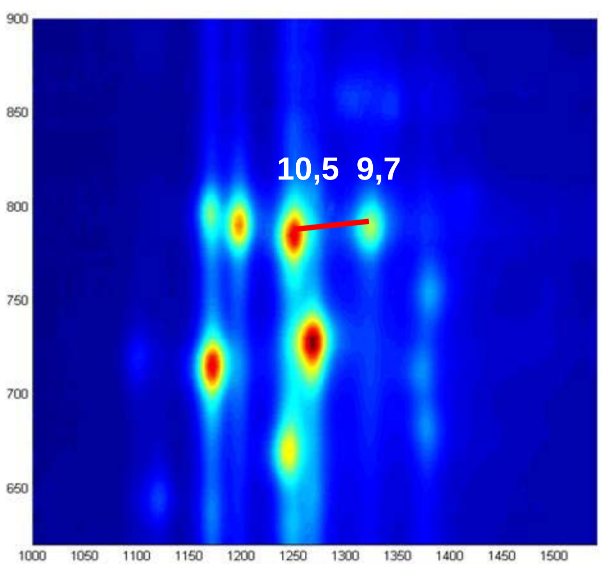
Discriminate semiconducting tubes with the help of photoluminescense .

- **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.

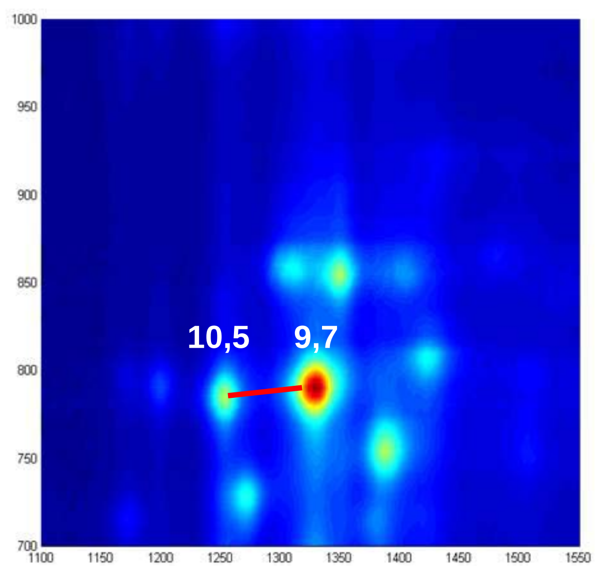
- Only 12 - 14 semiconducting tubes.

- In order to measure peak amplitudes precisely, each peak is fitted wit 2-d Lorentzian

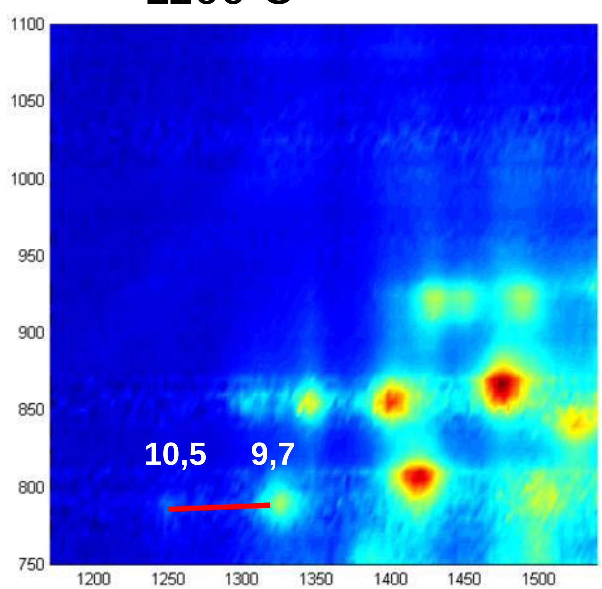
900 C



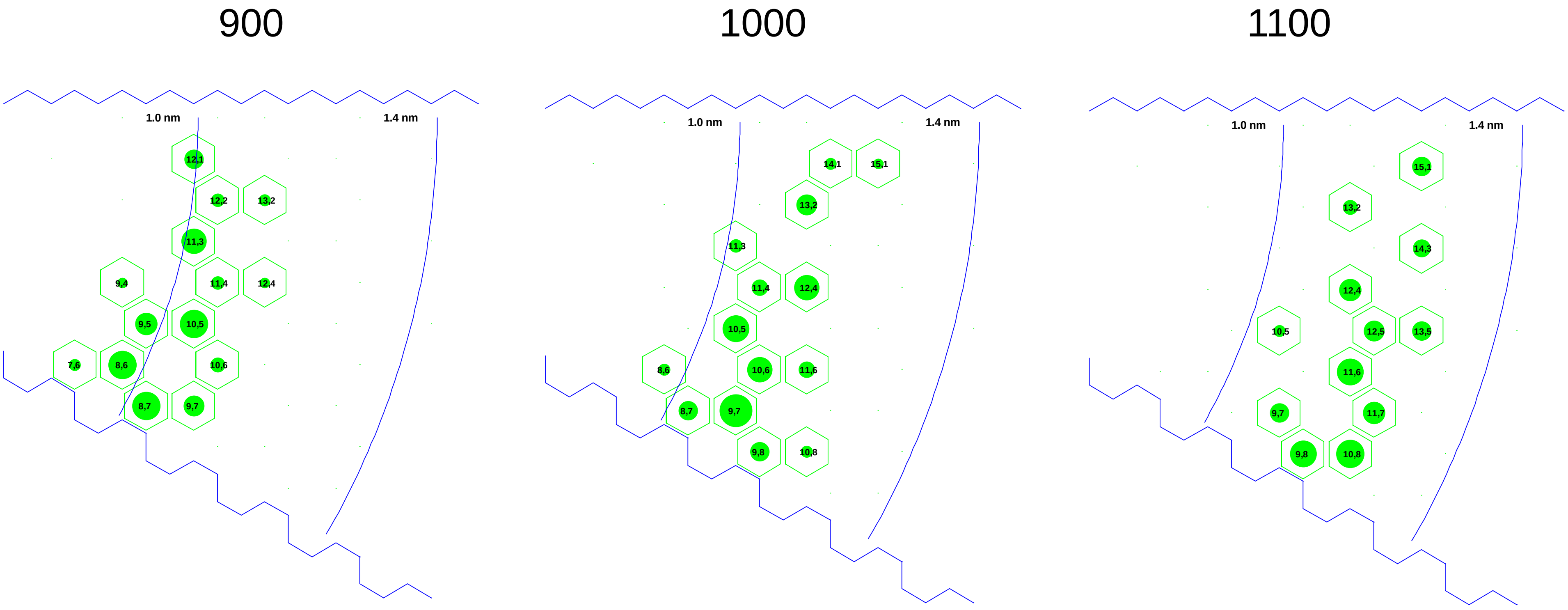
1000 C



1100 C



Resulting chiral maps: semiconductors only



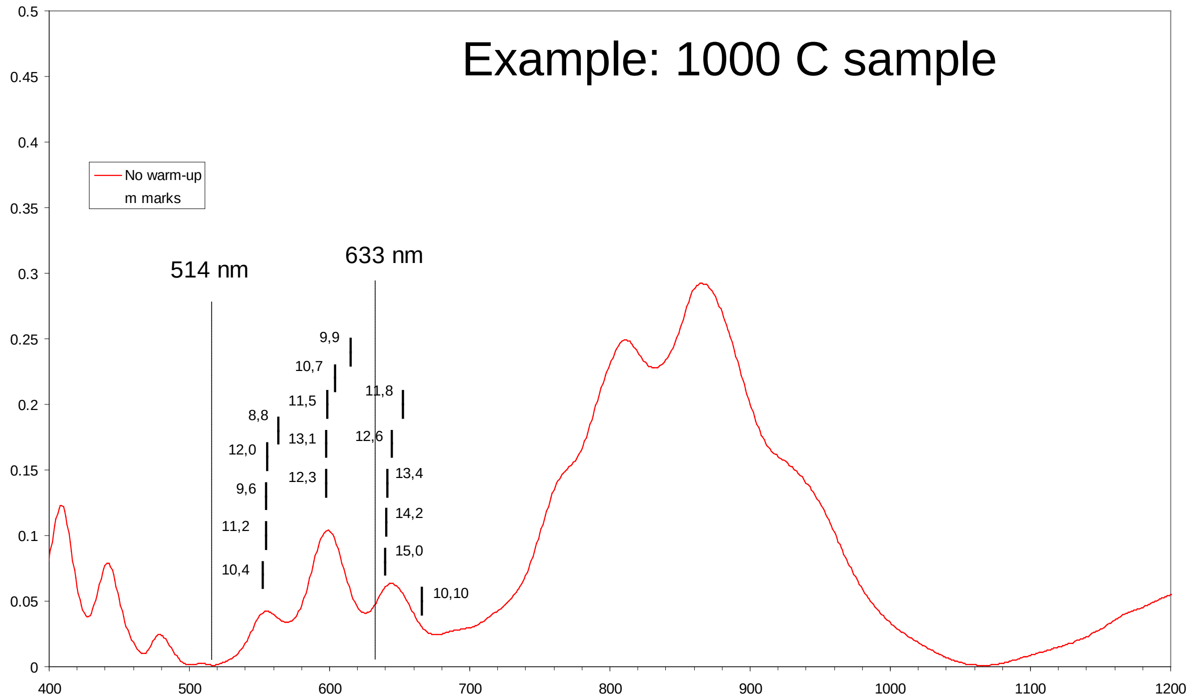
Metallic tubes: no PL makes similar analysis impossible.

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

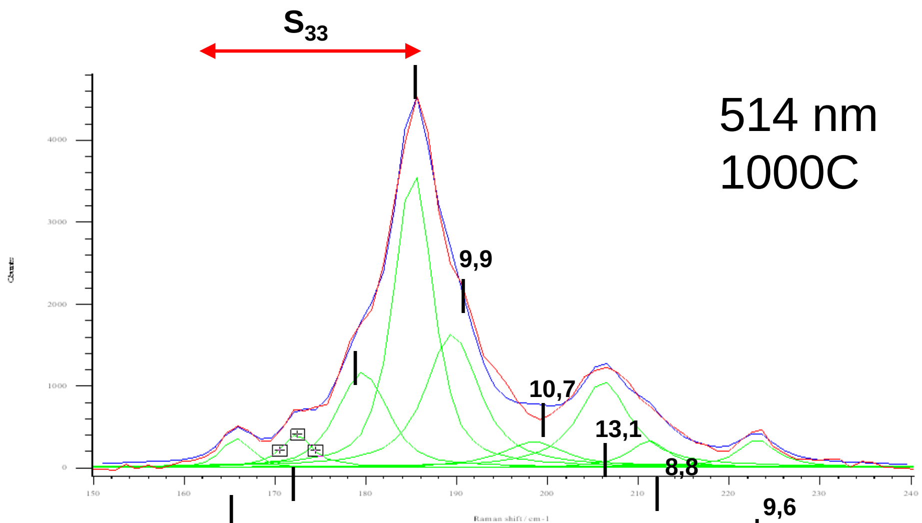
Raman: 514 nm excitation is reasonably in tune with first peak. Will also excite large diameter semiconductors on S_{33} transition

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

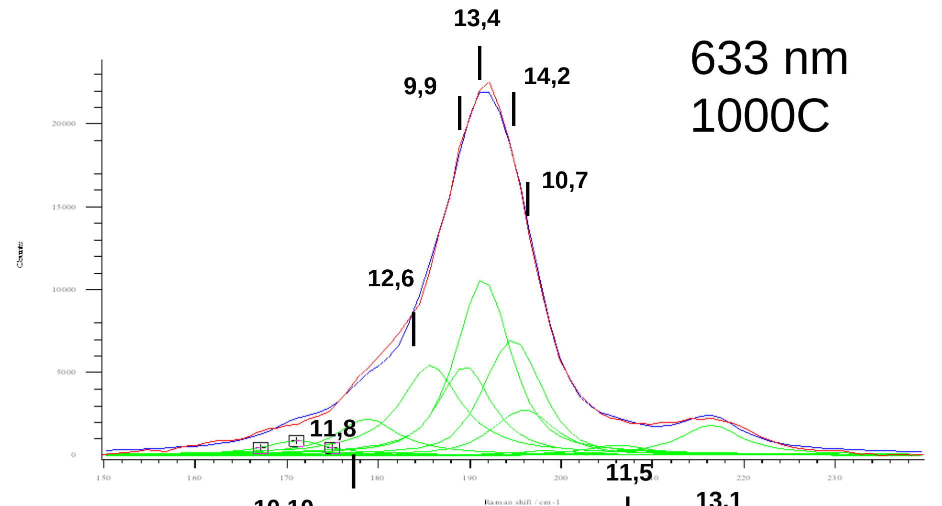
RBM frequencies are much better known and reproducible.



Raman spectra deconvolution

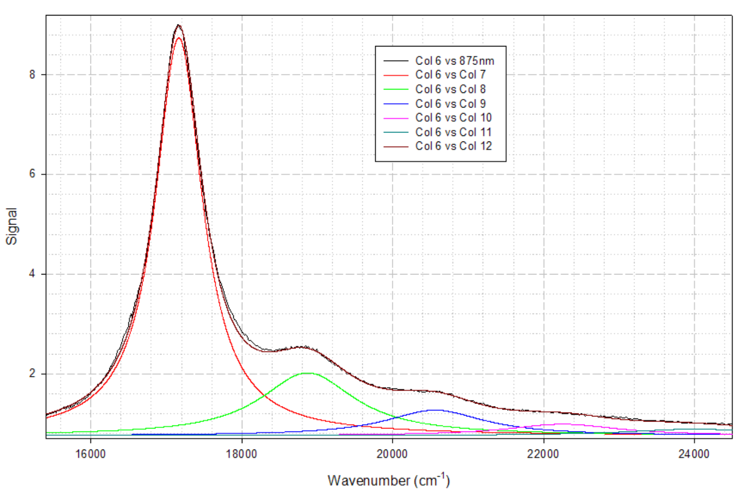


Curve Name	Centre	Width	Height	% Gaussian	Type	Area
9,6	223.2	5	337.709	3.65367	Mixed	2621.13
12 3	212.8	5	41.1601	1.63329	Mixed	321.568
8 8	211.2	5	328.103	11.2182	Mixed	2483.74
13,1	216.1	5	44.8677	100	Mixed	238.801
11,5	206.2	7	1051.06	9.72749	Mixed	11194.6
10,7	198.5	8	317.164	0	Mixed	3985.6
9,9	189.5	7	1644.66	18.9685	Mixed	16978.3
Curve 8	185.223	5.24104	3626.77	40.3684	Mixed	25972.6
Curve 9	179.581	6.65556	1176.16	45.2136	Mixed	10504.1
Curve 10	165.711	4	349.521	50.6419	Mixed	1837.62
Curve 11	172.38	4	406.88	1.86818	Mixed	2541.1



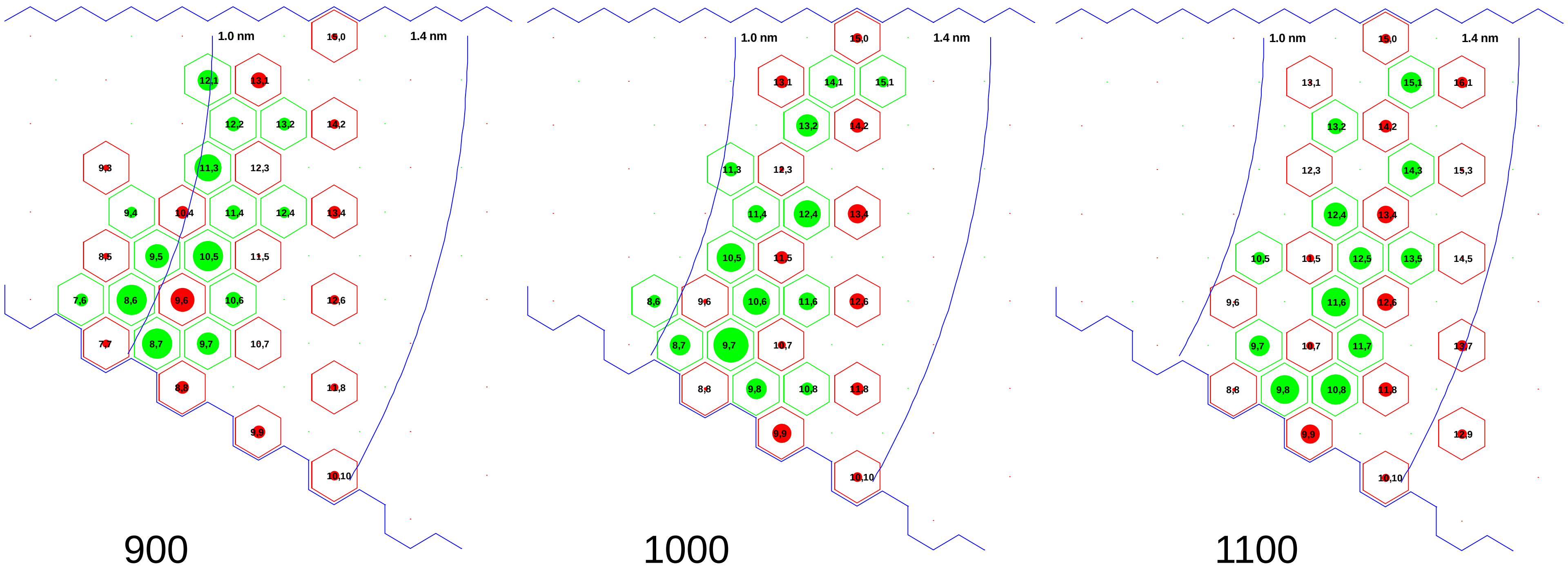
Curve Name	Centre	Width	Height	% Gaussian	Type	Area
12 3	212.8	5	117.901	0.525304	Mixed	924.423
13,1	216.5	8	1827.16	8.87517	Mixed	22304
11,5	206.2	7.6021	602.688	12.8479	Mixed	6898.85
10,7	198.5	8	251.175	0	Mixed	3156.35
9,9	189.5	7	5390.14	20.9555	Mixed	55264.2
15,0	195.9	8	2738.15	41.4336	Mixed	29813.1
14,2	194.7	7.42744	7010.72	48.8052	Mixed	68926.4
13,4	191.5	7.08429	10721	34.772	Mixed	105931
12,6	185.7	8	5484.83	1.26744	Mixed	68642.8
11,8	178.8	7.98771	2192.55	0.102185	Mixed	27501
10,10	171	8	874.503	0	Mixed	10989.3

Excitation for 875 nm emission



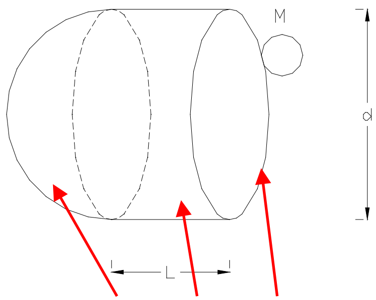
Excitation is off-resonance:
Use excitation profile and assume that linewidth and overtone tail scale with the transition energy
RBM frequencies are known to shift due to bundling, etc. However it is possible to find an “ancor” tube ((9,6), (13,1) in this case) and determine the RBM frequencies of the other tubes

Resulting chiral maps: semiconductors AND metallics.

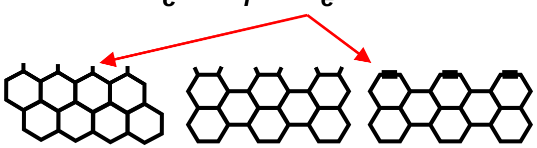


The larger diameter tubes have chiral angles closest to arm-chair (30^{o})

Does this observation agree with the nucleation model?



$$E = E_c + E_r + E_e$$



ε_e zig-zag > ε_e armchair

$\boldsymbol{E_c}$, is to a good approximation independent of tubulet radius (determined by 5 pentagons in a hemisphere).

$\boldsymbol{E_r = \varepsilon_r L/R}$, **where** ε_r is bending ***stiffness of a graphene sheet, L*** is length of the cylinder, and ***R*** is tubulet radius.

$\boldsymbol{E_e = 2\pi R \varepsilon_e}$, where ε_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:

$$R \sim (N\varepsilon_r / \varepsilon_e)^{1/3}.$$

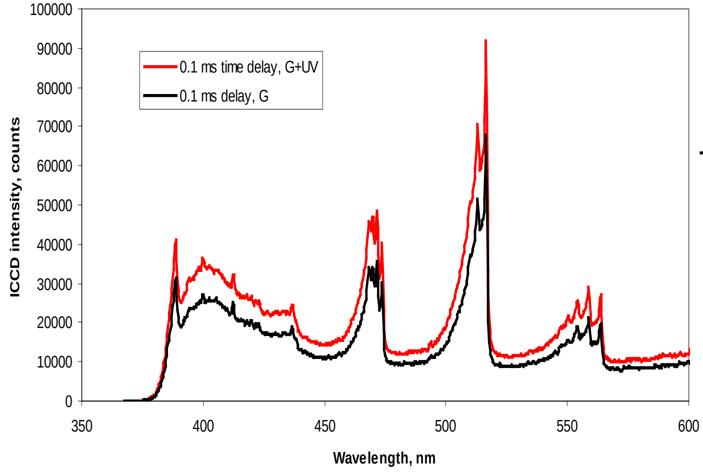
Therefore, decrease in the edge energy ε_e will lead to increase in the diameter of a nanotube nucleus.

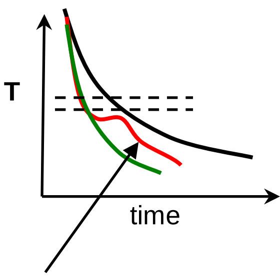
If ε_e armchair < ε_e zig-zag, nuclei with the edge closest to arm-chair structure will nucleate largest diameter nanotubes.

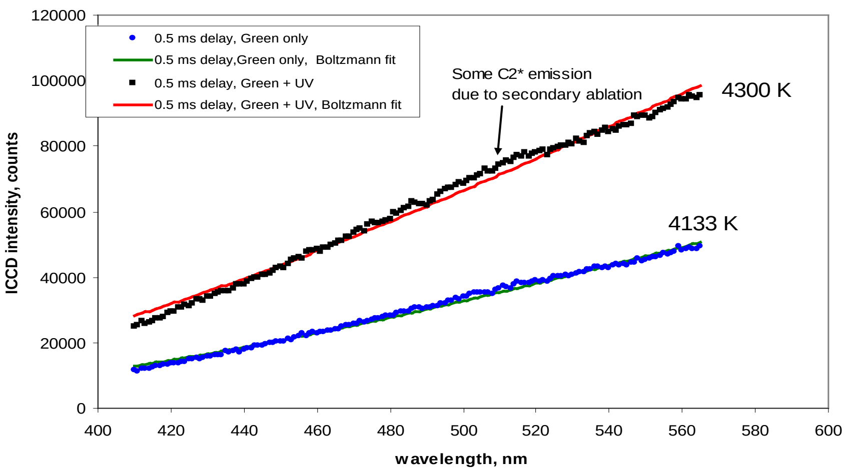
A. Thess, R. Lee, P. Nikolaev, H. J. Dai, P. Petit, J. Robert, C. H. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer, and R. E. Smalley, *Science* 273, 483 **(1996)**.

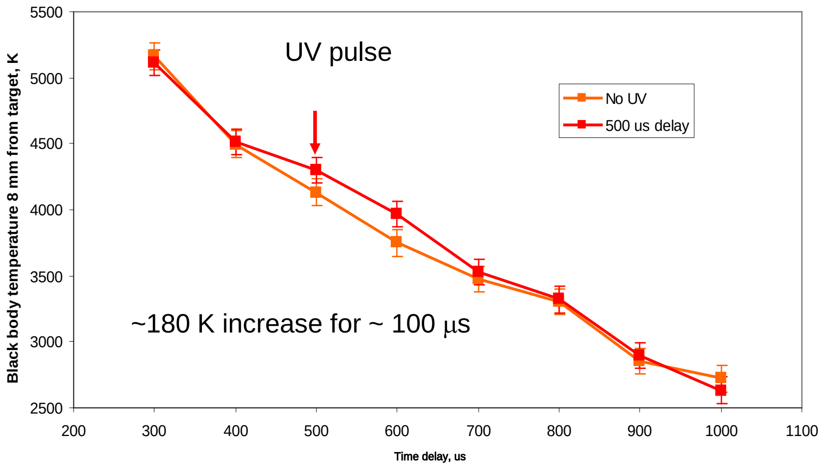
“Warm-up” approach: what should be the energy density and time delay?

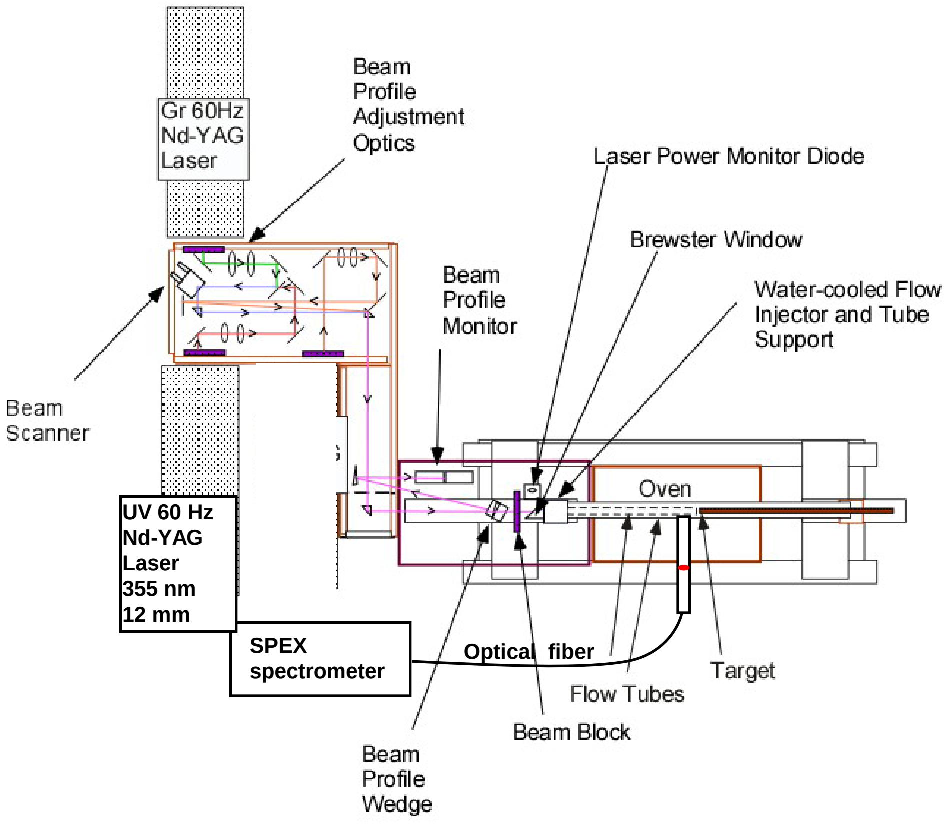
Time delay: 500 μs. (decided rather arbitrarily)
Energy density:
Green energy: 1.6 J/cm^2
-UV: avoid secondary ablation
-UV energy varied, looking at increase in C_2^* emission on top of black body continuum. Secondary ablation threshold ~0.1 J/cm^2 for 500μs delay.
Oven temperature: 1000 ºC. We need to bring SWCNT diameter within the reach of spectroscopy tools.











Nanotube population: is it enriched in armchair structures as a result?

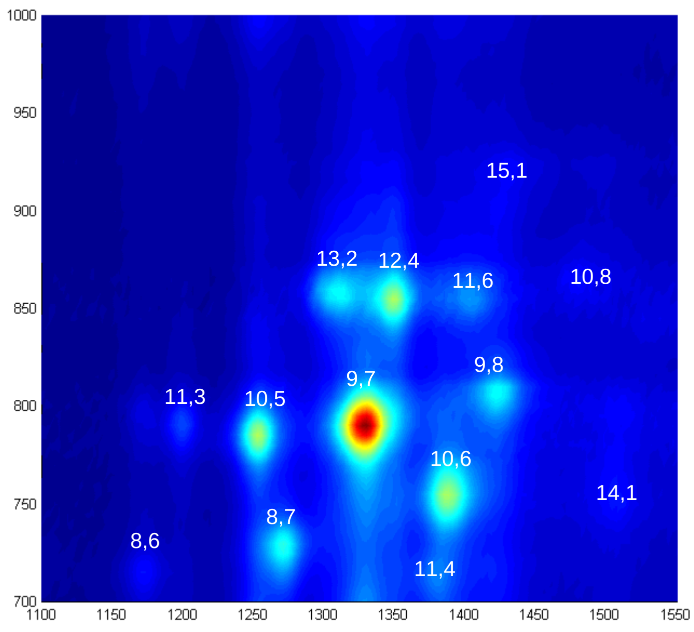
Discriminate semiconducting tubes with the help of photoluminescense .

•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.

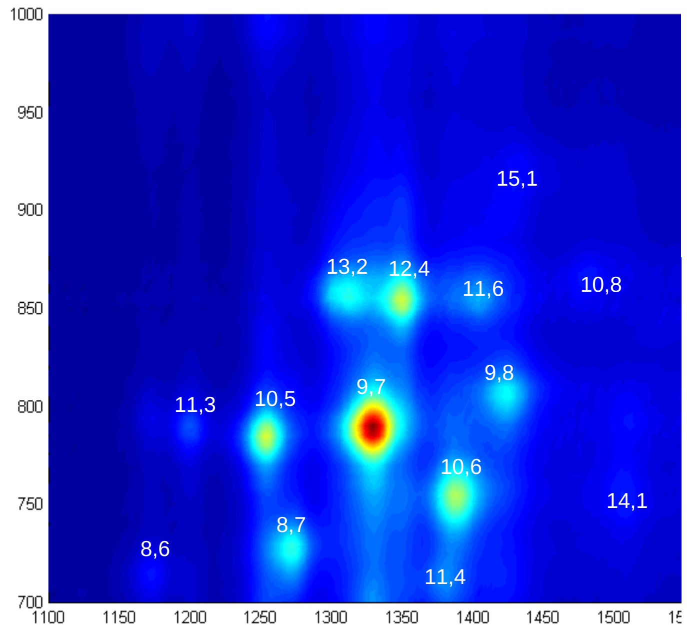
•Only 14 semiconducting tubes.

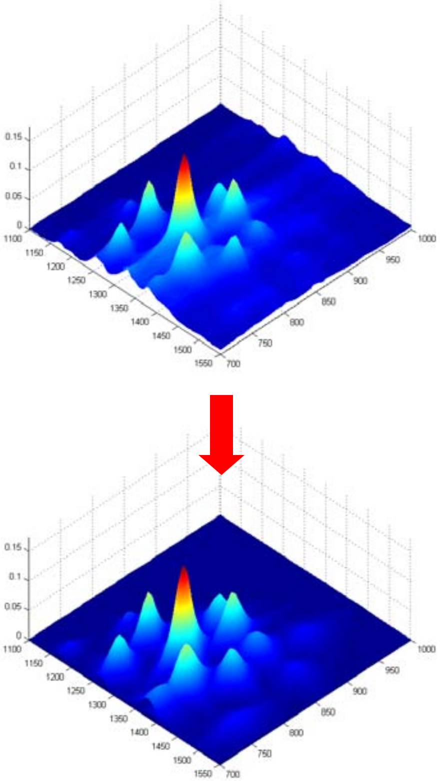
•Maps appear similar. In order to measure small differences, each peak is fitted wit 2-d Lorentzian

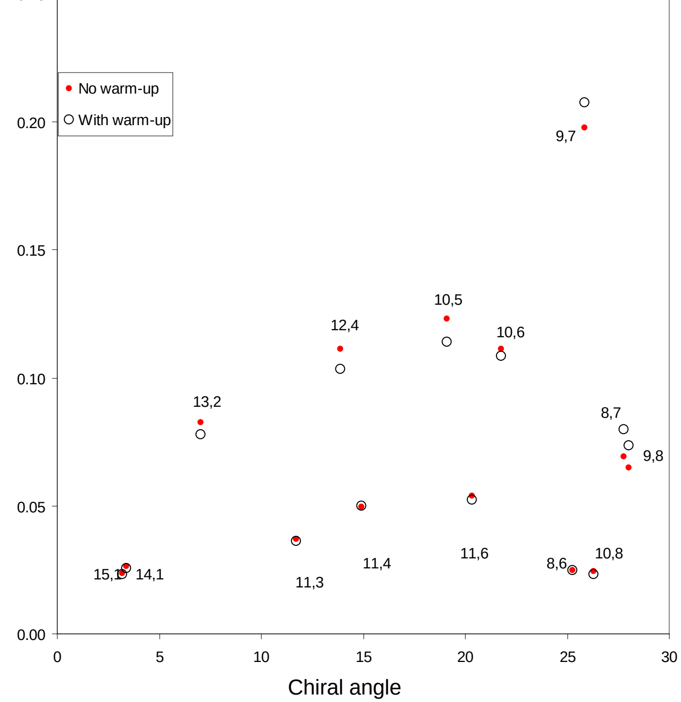
No warm-up



With warm-up







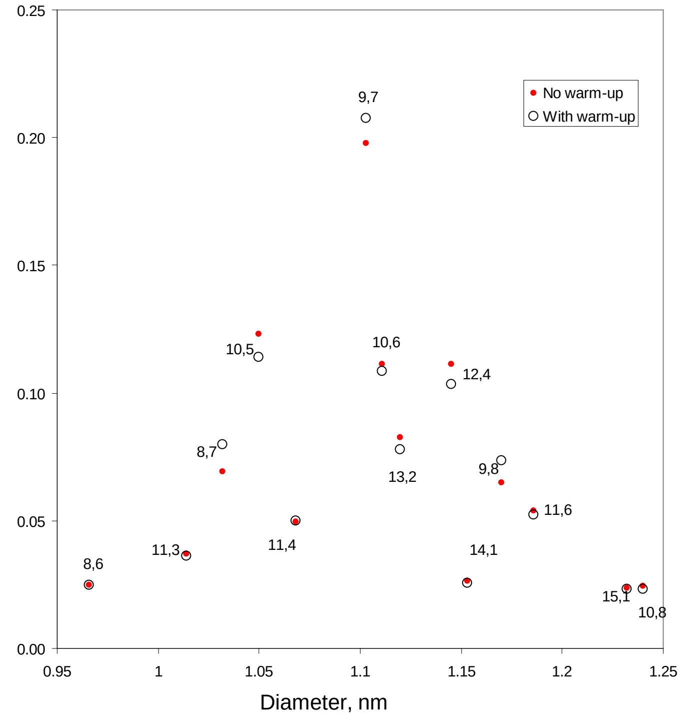
PL data:

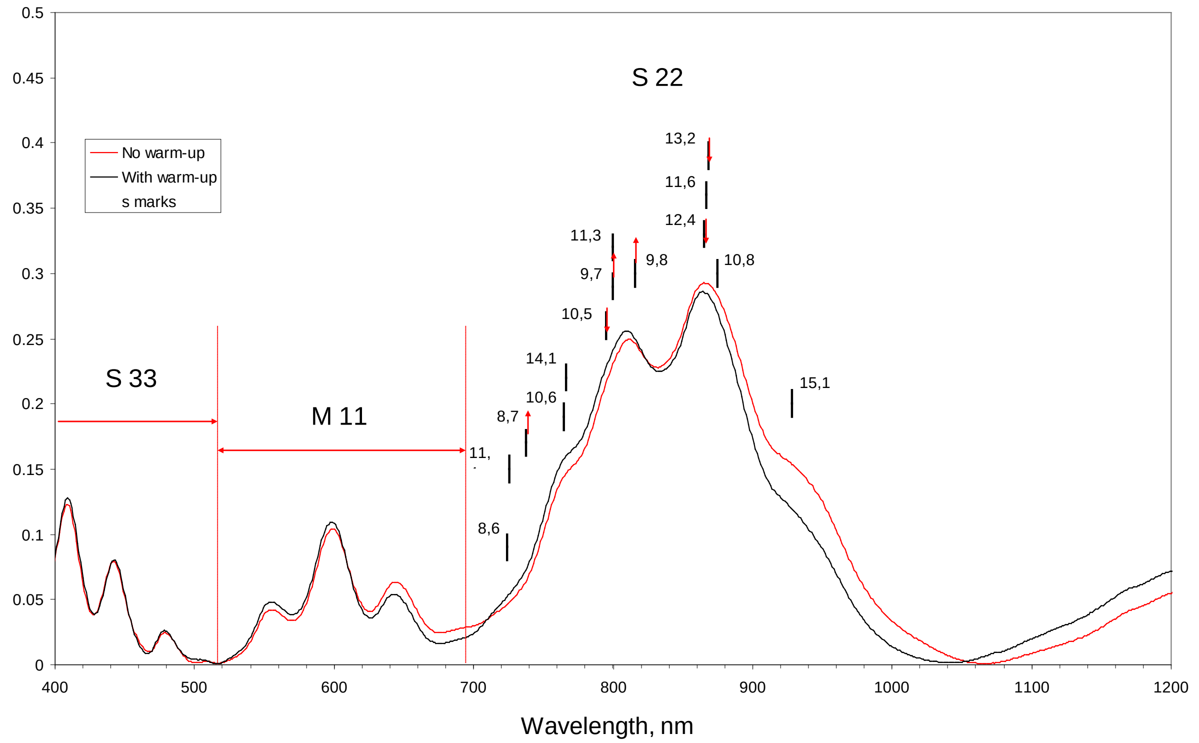
(9,7), (9,8), and (8,7) increase with warm-up
-all have chiral angles >25º, close to armchair

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

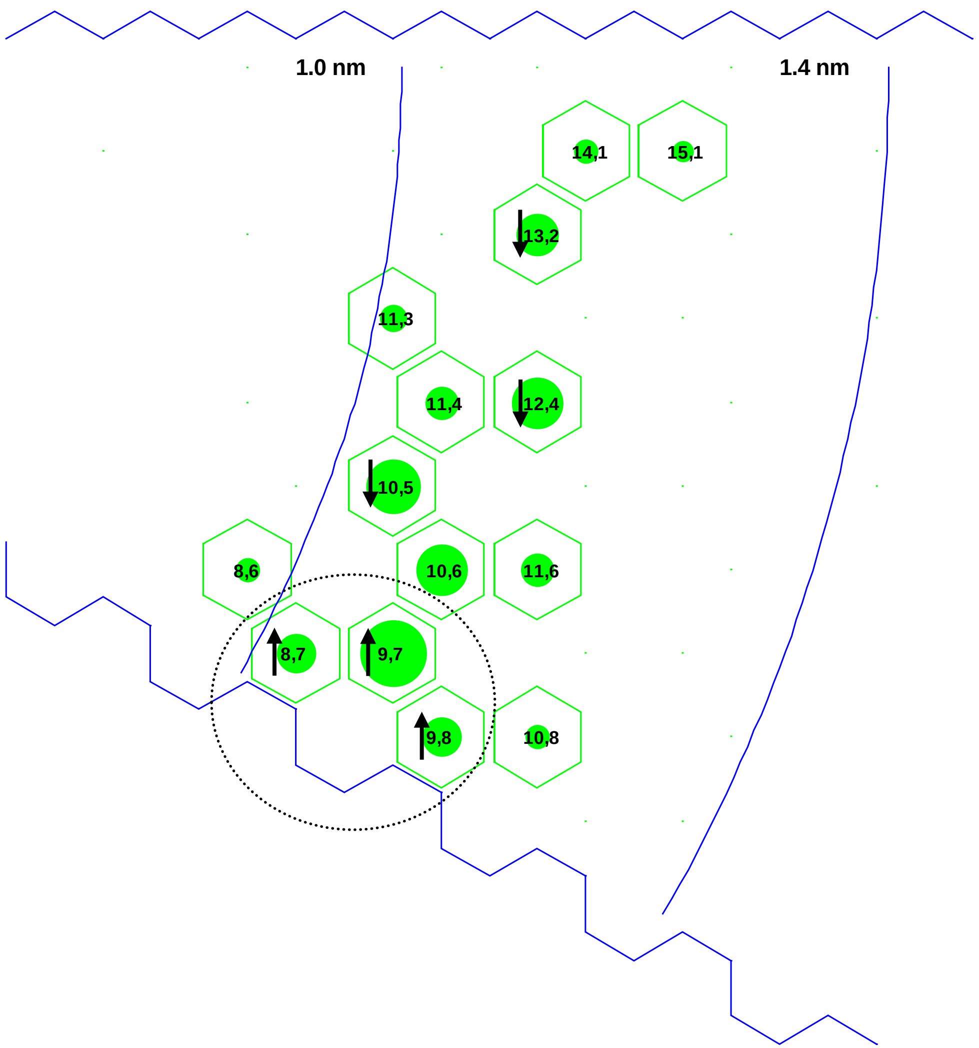
No clear diameter dependence

Absorption data is consistent with this.



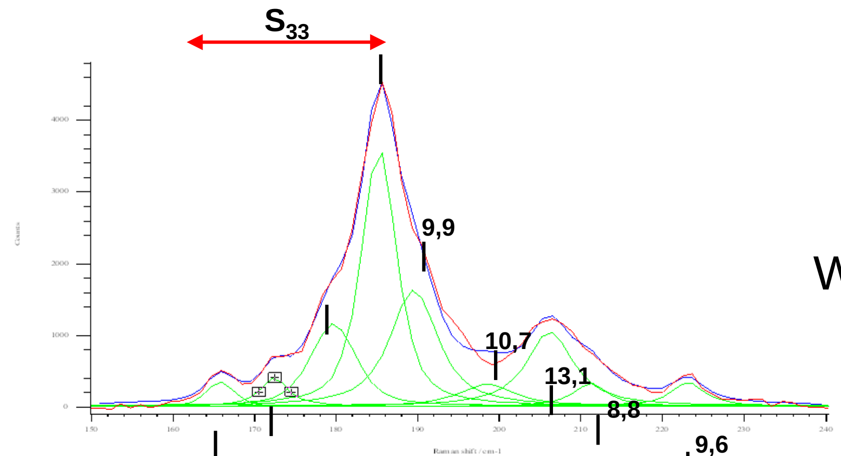


Chiral map.

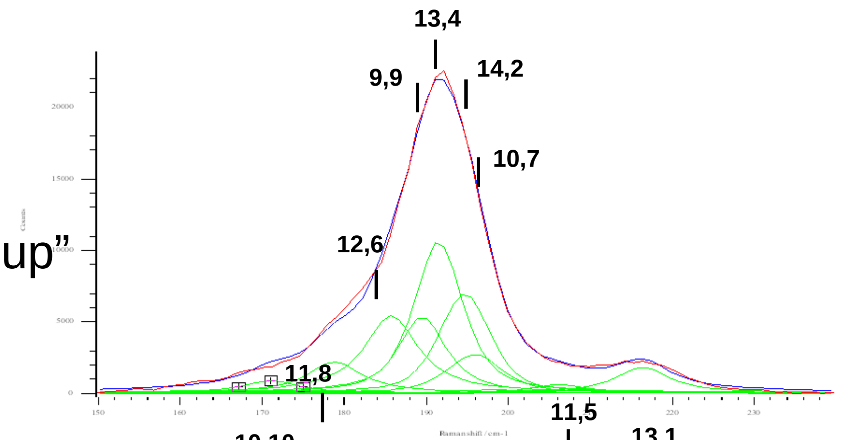


514 nm | Raman spectra deconvolution | 633 nm

With “warm-up”

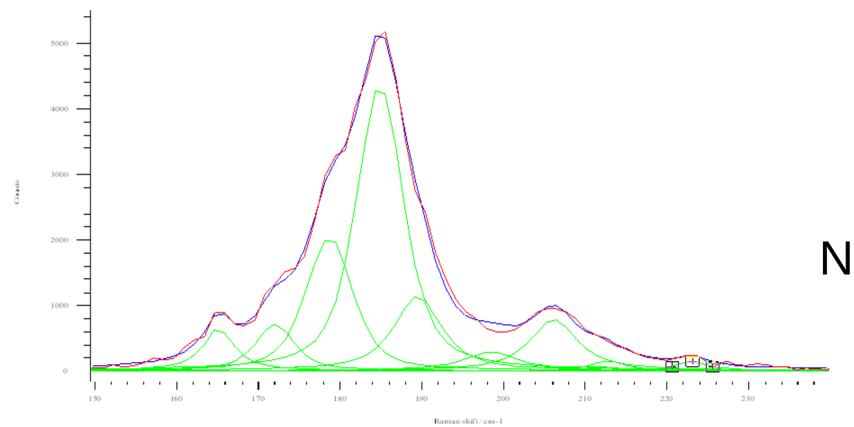


Curve Name	Centre	Width	Height	% Gaussian	Type	Area
9,6	223.2	5	337.709	3.65367	Mixed	2621.13
12 3	212.8	5	41.1601	1.63329	Mixed	321.568
8 8	211.2	5	328.103	11.2182	Mixed	2483.74
13,1	216.1	5	44.8677	100	Mixed	238.801
11,5	206.2	7	1051.06	9.72749	Mixed	11194.6
10,7	198.5	8	317.164	0	Mixed	3985.6
9,9	189.5	7	1644.66	18.9685	Mixed	16978.3
Curve 8	185.223	5.24104	3626.77	40.3684	Mixed	25972.6
Curve 9	179.581	6.65556	1176.16	45.2136	Mixed	10504.1
Curve 10	165.711	4	349.521	50.6419	Mixed	1837.62
Curve 11	172.38	4	406.88	1.86818	Mixed	2541.1

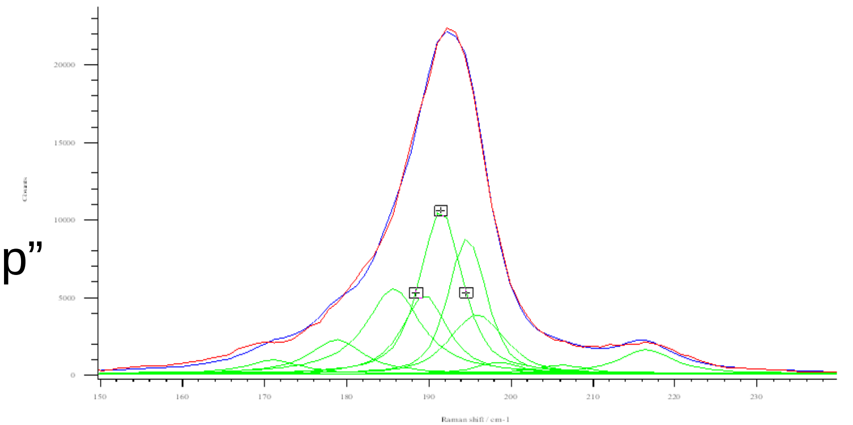


Curve Name	Centre	Width	Height	% Gaussian	Type	Area
12 3	212.8	5	117.901	0.525304	Mixed	924.423
13,1	216.5	8	1827.16	8.87517	Mixed	22304
11,5	206.2	7.6021	602.688	12.8479	Mixed	6898.85
10,7	198.5	8	251.175	0	Mixed	3156.35
9,9	189.5	7	5390.14	20.9555	Mixed	55264.2
15,0	195.9	8	2738.15	41.4336	Mixed	29813.1
14,2	194.7	7.42744	7010.72	48.8052	Mixed	68926.4
13,4	191.5	7.08429	10721	34.772	Mixed	105931
12,6	185.7	8	5484.83	1.26744	Mixed	68642.8
11,8	178.8	7.98771	2192.55	0.102185	Mixed	27501
10,10	171	8	874.503	0	Mixed	10989.3

No “warm-up”

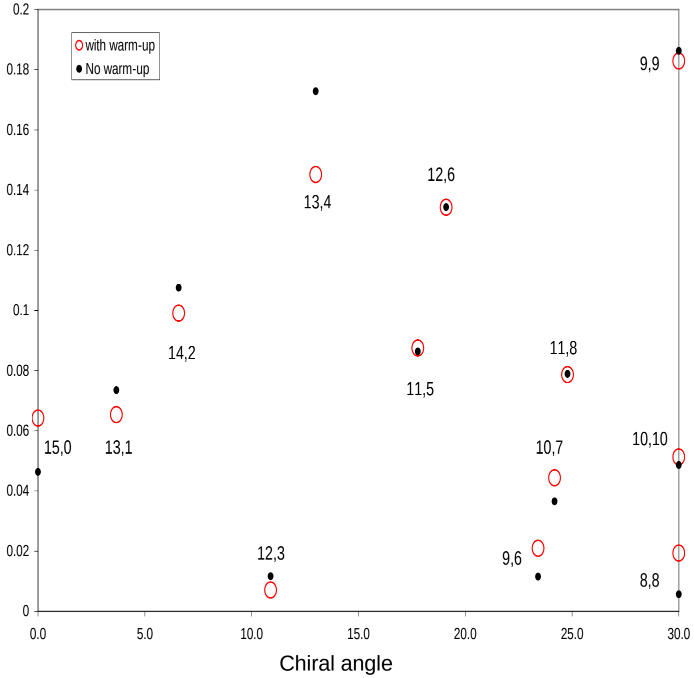


Curve Name	Centre	Width	Height	% Gaussian	Type	Area
9,6	223.2	5	140.077	0	Mixed	1100.16
12 3	212.8	5	150.674	9.29544	Mixed	1147.93
8 8	211.2	5	71.2357	1.57858	Mixed	556.637
13,1	216.1	5	37.0412	0	Mixed	290.921
11,5	206.2	7	790.806	7.90308	Mixed	8473.85
10,7	198.5	8	291.213	0	Mixed	3659.49
9,9	189.5	7	1146.51	17.2191	Mixed	11906.9
Curve 8	184.885	6.94362	4410.06	40.8448	Mixed	41767.8
Curve 9	178.671	6.846	2052.74	46.3776	Mixed	18774.5
Curve 10	171.991	5.644	719.189	32.1712	Mixed	5714.83
Curve 11	165.079	4.51719	654.533	0.591797	Mixed	4635.44



Curve Name	Centre	Width	Height	% Gaussian	Type	Area
12 3	212.8	8	131.316	0	Mixed	1650.17
13,1	216.5	8	1631.45	0	Mixed	20501.4
11,5	206.2	8	598.444	10.7369	Mixed	7260
10,7	198.5	6.54025	790.484	0	Mixed	8120.95
9,9	189.5	6.53266	5150.22	19.6121	Mixed	49507.9
15,0	195.9	8	3887.91	41.5306	Mixed	42316.4
14,2	194.7	5.51341	8899.75	48.2744	Mixed	65082.2
13,4	191.5	6.1246	10674	34.7181	Mixed	91197.4
12,6	185.7	8	5605.12	0.369352	Mixed	70352.2
11,8	178.8	7.91026	2263	0.15567	Mixed	28104.6
10,10	171	8	945.788	0	Mixed	11885.1

Raman data:



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

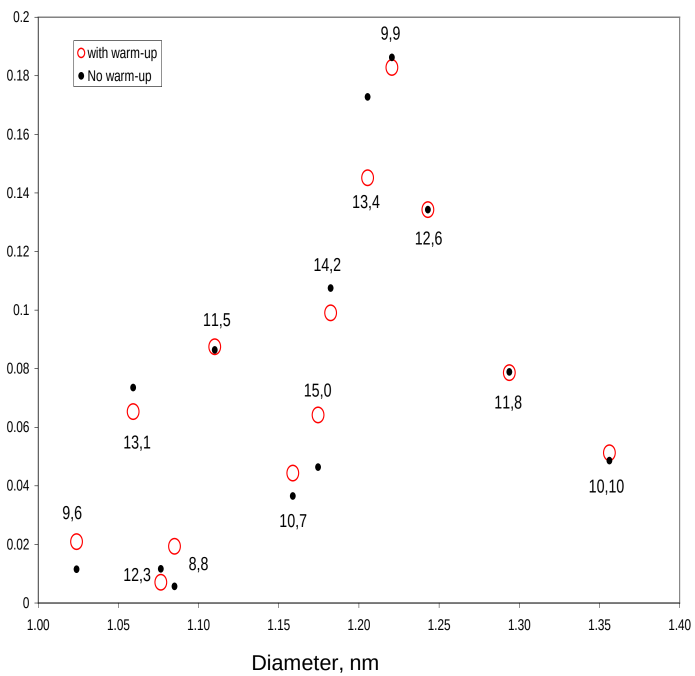
(12,6), (11,5), (13,4) and (14,2) decrease with warm-up
-all have chiral angles <20º

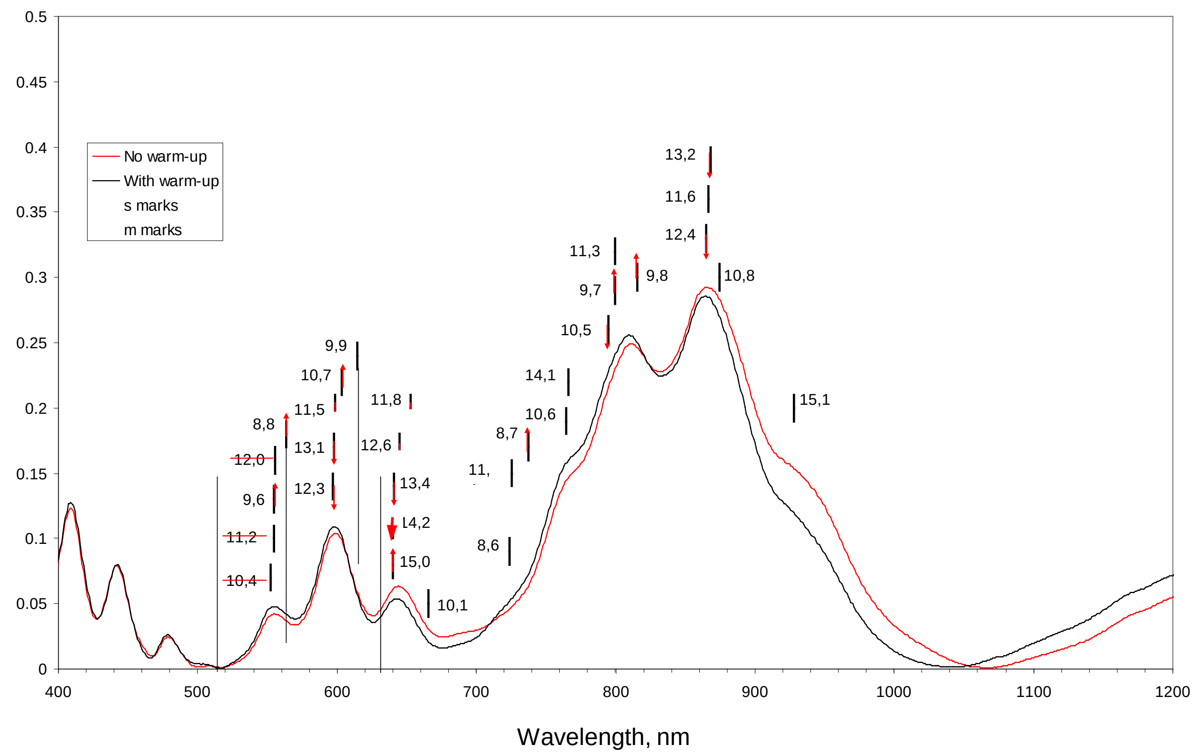
(9,9) did not change

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

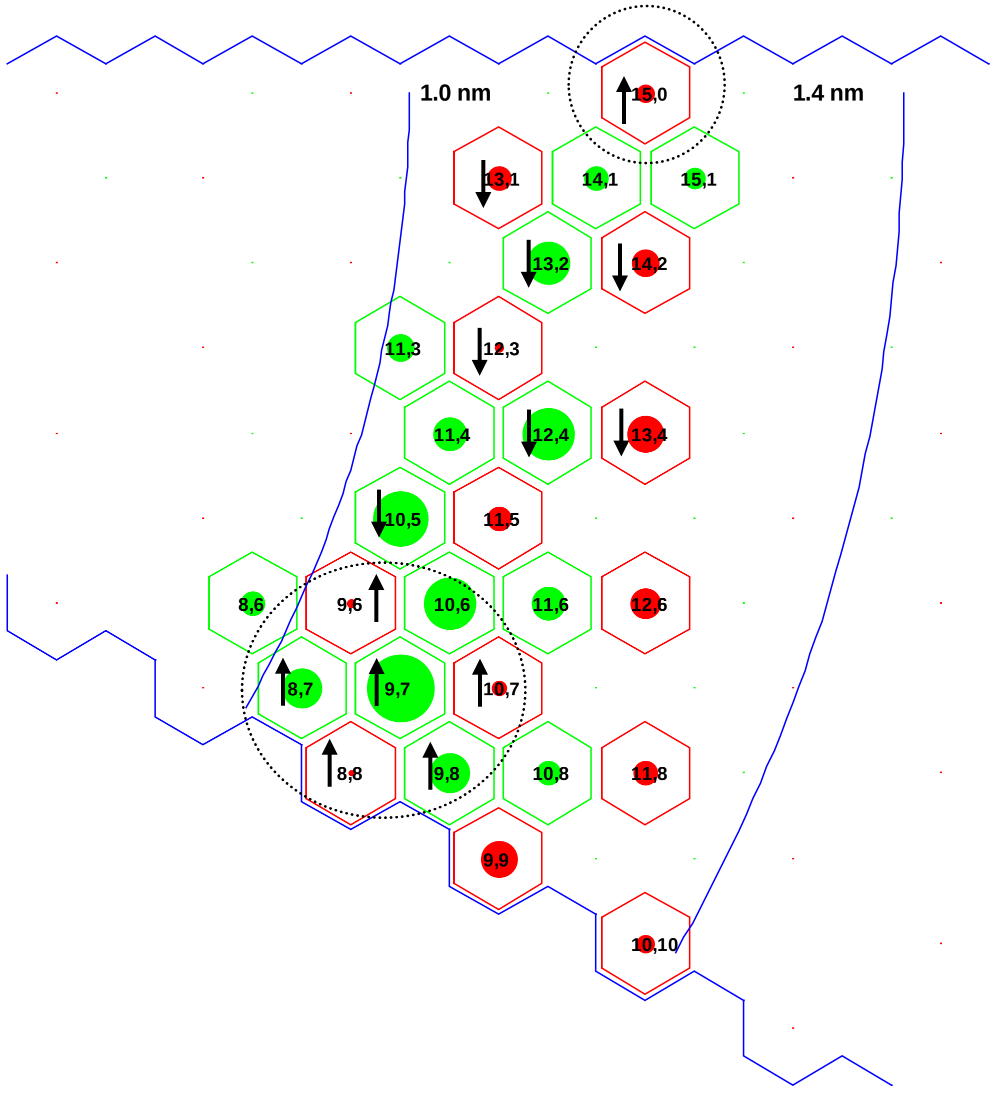
No clear diameter dependence

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





Chiral map.



1.0 nm
1.4 nm
15,0
13,1
14,1
15,1
13,2
14,2
11,3
12,3
11,4
12,4
13,4
10,5
11,5
8,6
9,6
10,6
11,6
12,6
8,7
9,7
10,7
8,8
9,8
10,8
11,8
9,9
10,10

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.