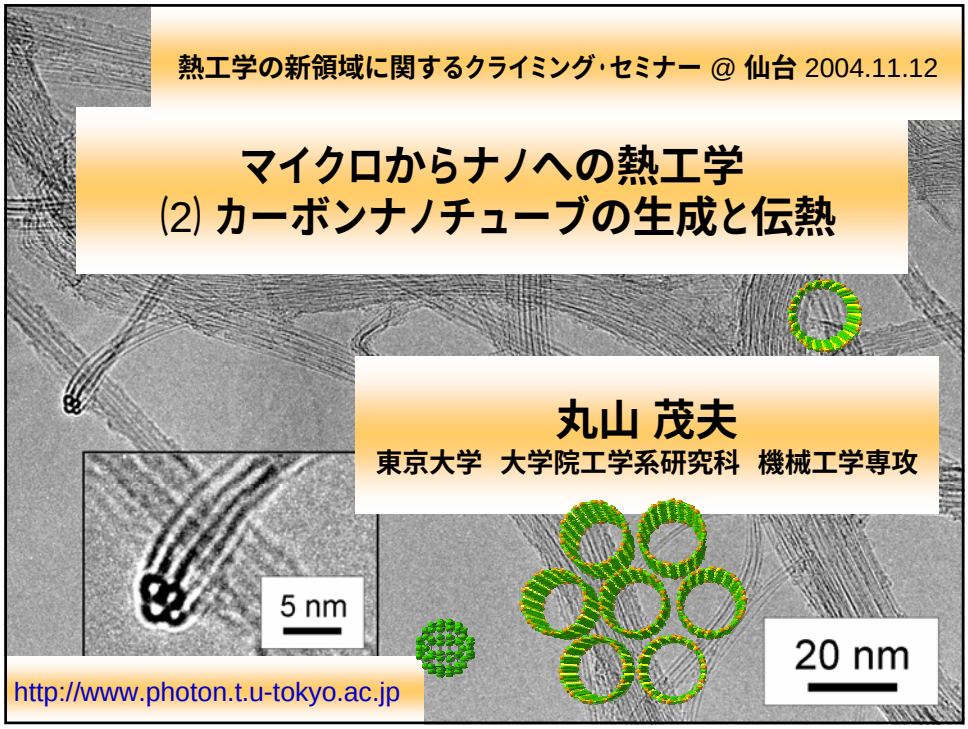
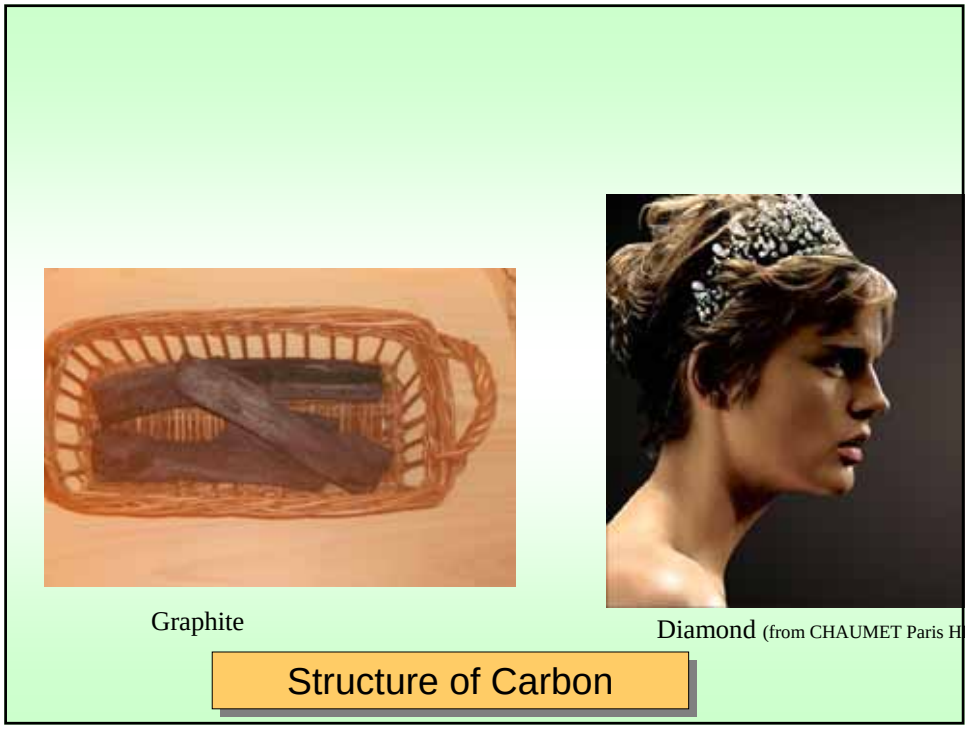
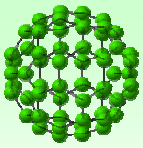
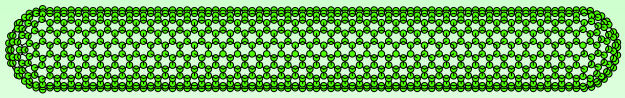

熱工学の新領域に関するクライミング･セミナー @ 仙台 2004.11.12
マイクロからナノへの熱工学
(2) カーボンナノチューブの生成と伝熱
丸山 茂夫
東京大学　大学院工学系研究科　機械工学専攻
5 nm
20 nm
http://www.photon.t.u-tokyo.ac.jp

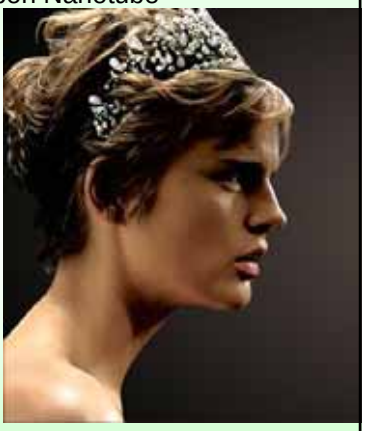

Graphite
Diamond (from CHAUMET Paris H
Structure of Carbon





1-D: Carbon Nanotube

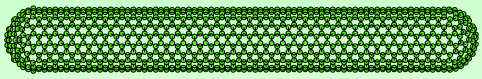
0-D: Fullerene



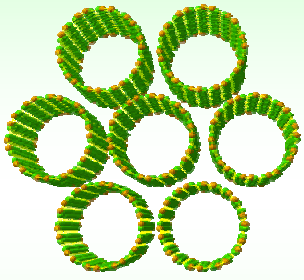
Graphite

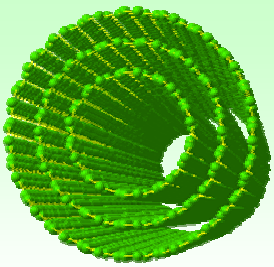
Diamond (from CHAUMET Paris H

Structure of Carbon

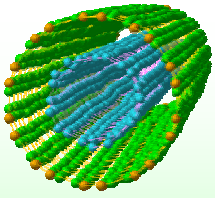


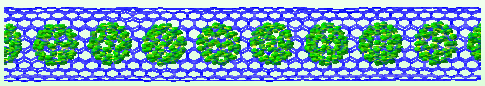
Single-Walled Carbon Nanotube, SWNT





Multi-Walled Carbon Nanotubes
MWNT



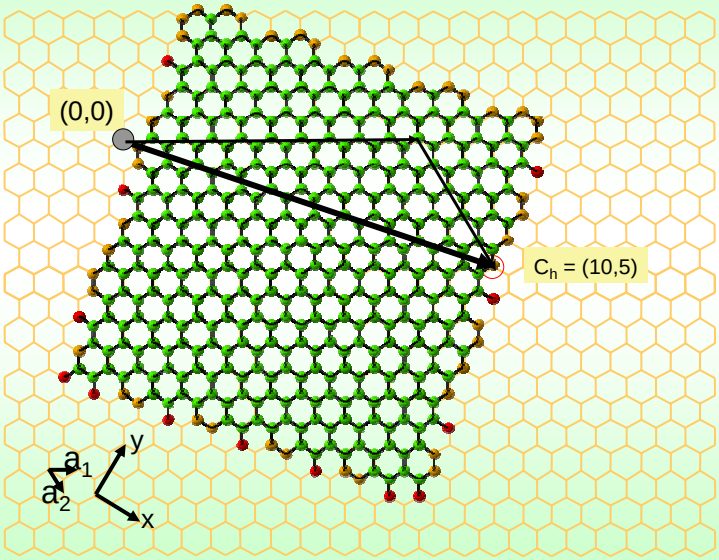


Peapod

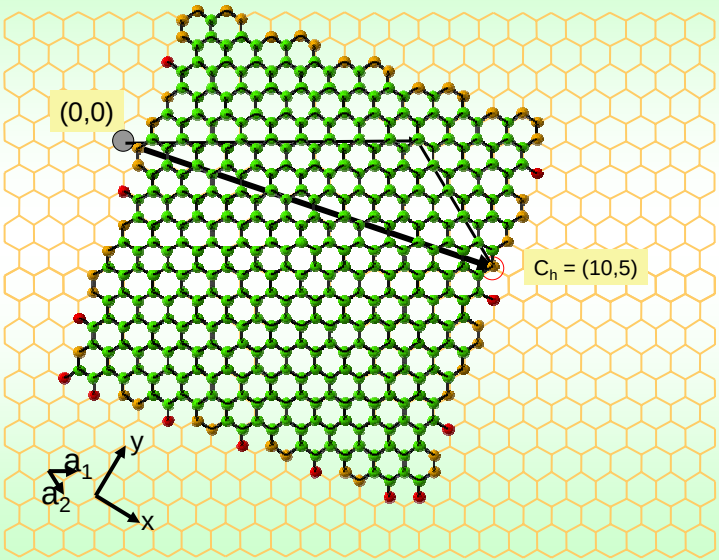
Double-Walled Carbon Nanotubes
DWNT

Carbon Nanotubes

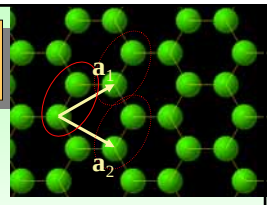
Wrapping (10,5) SWNT (chiral)

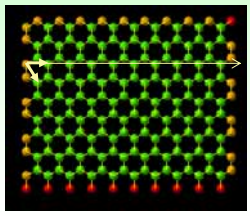


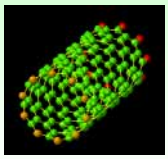
Wrapping (10,5) SWNT (chiral)



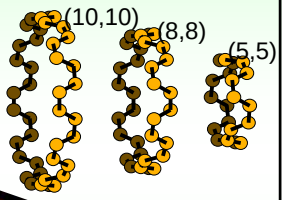
Chirality and Radius of SWNT

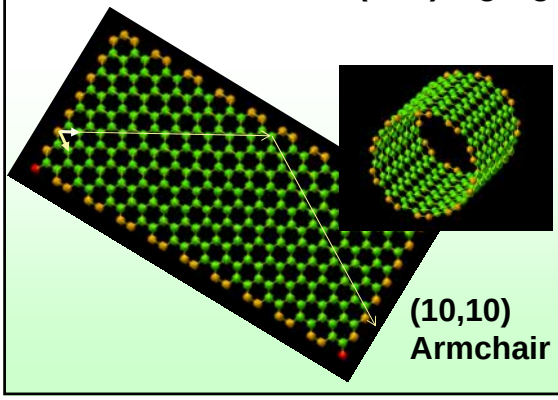




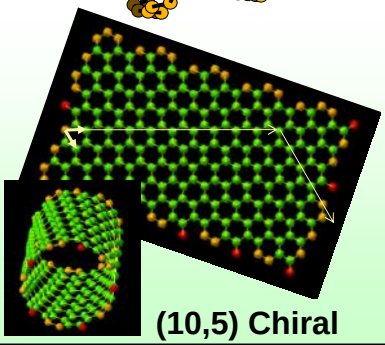


(10,0) Zigzag



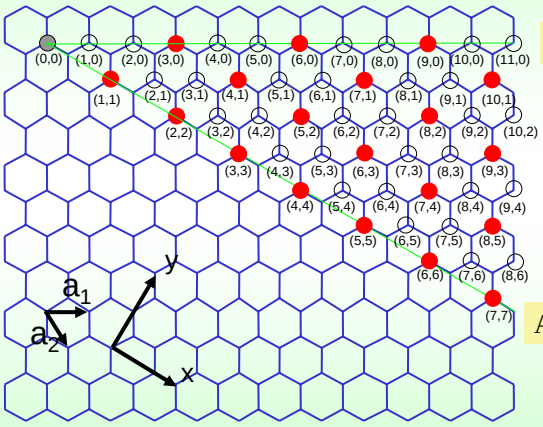


(10,10) Armchair



(10,5) Chiral

Hexagonal Lattice (n,m) nanotubes

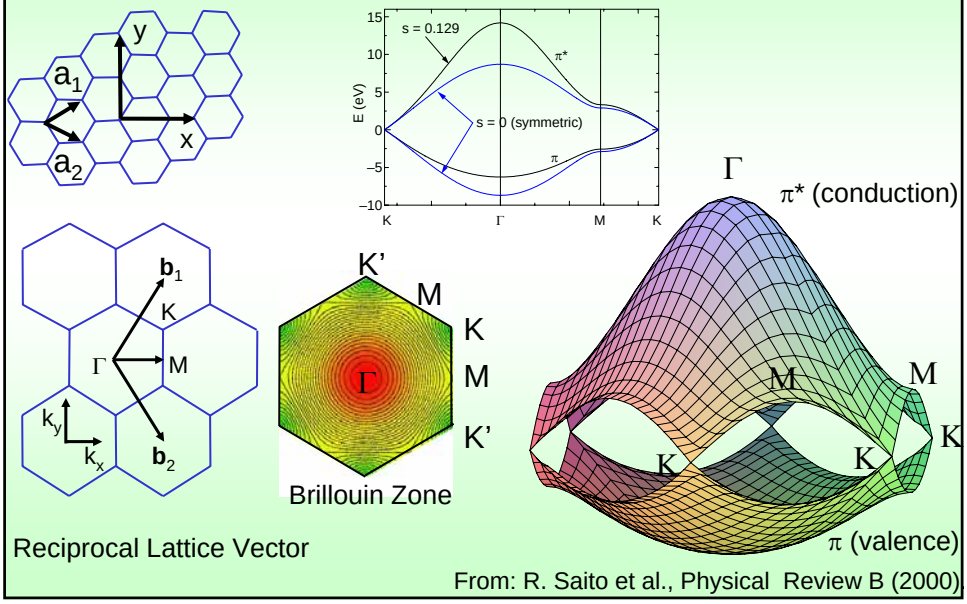


Zigzag

Armchair

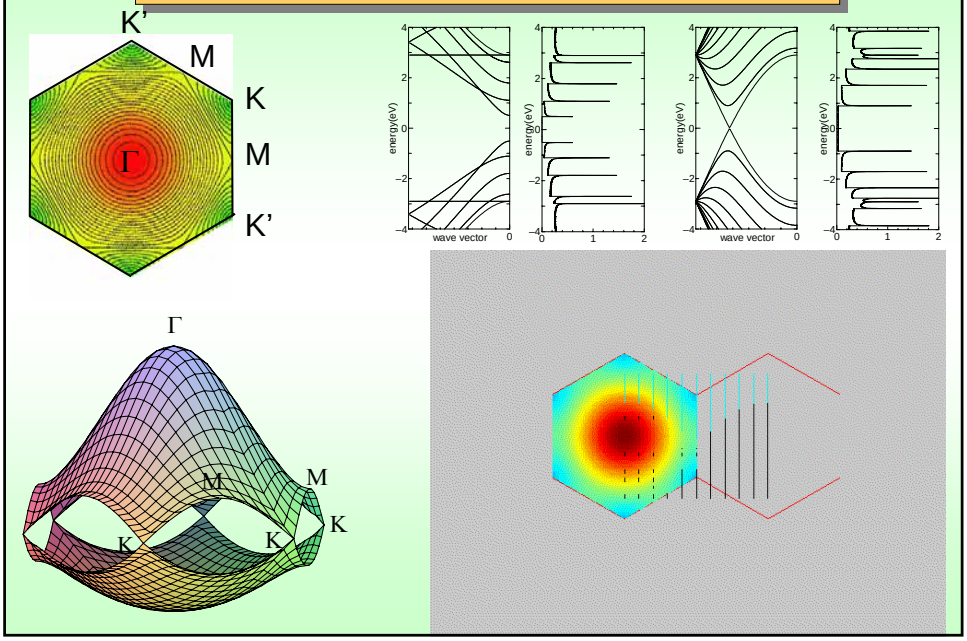
n - m = 3q (q: integer): metallic
n - m ≠ 3q (q: integer): semiconductor

2-D Energy dispersion relation for graphite



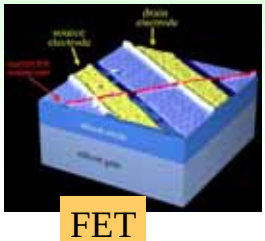
From: R. Saito et al., Physical Review B (2000)

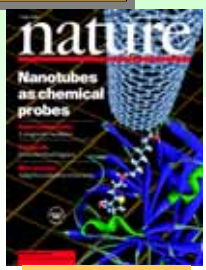
Electric DOS of Carbon Nanotube



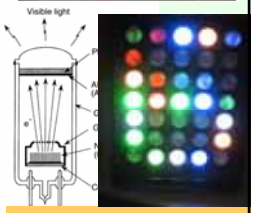
Application of Nanotubes

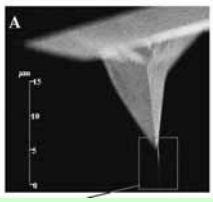
Nanowires


FET

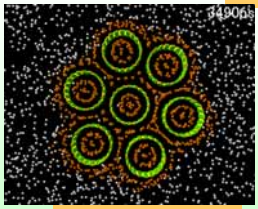


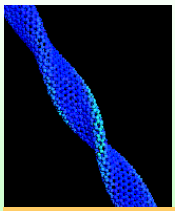
Biosensor



Field Emission


Tips of AFM

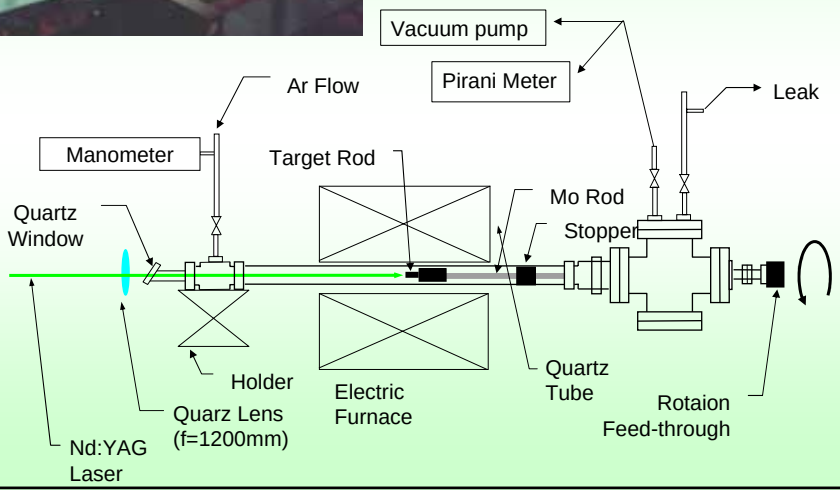

Fuel Cell Electrode


H2 Storage

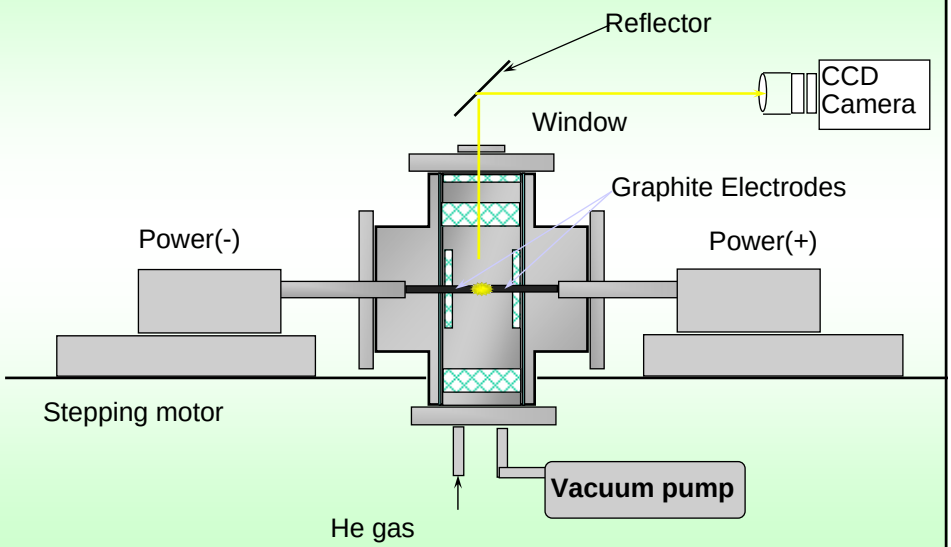

Mechanical

Generation of Single-Walled Carbon Nanotubes

Laser-Oven SWNT Generator



Arc-Discharge Generator



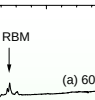
Alcohol CCVD on Catalysts Supported with Zeolite

Alcohol
Ethanol
Methanol

Electric Furnace

vacuum

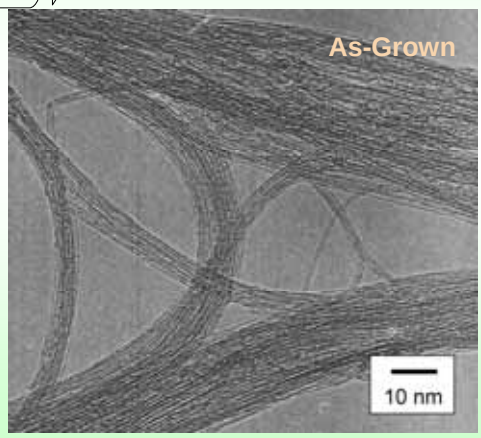
Simple, High-Purity
Low-Temperature
(550-900°C)



Shinohara & Nagy

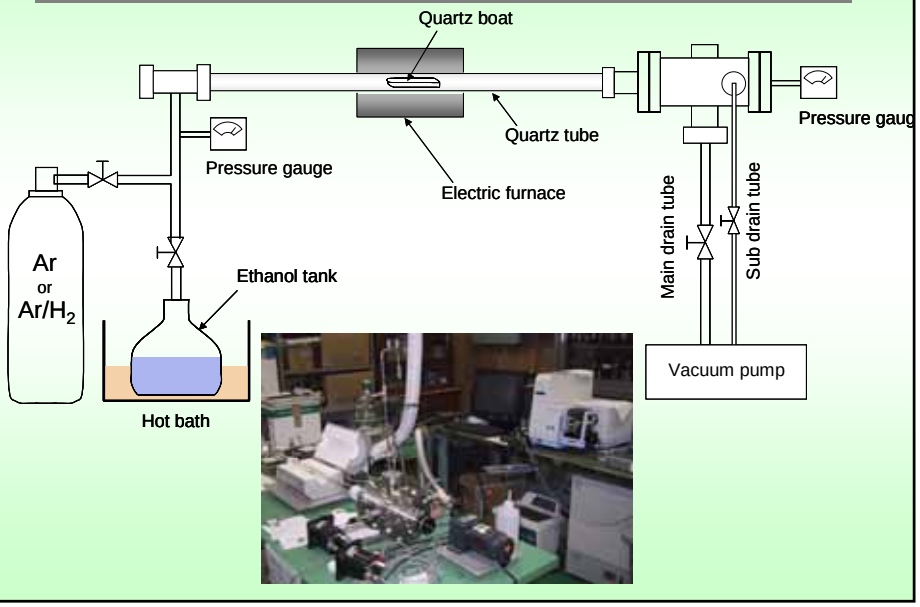
7.4[Å]

2.5/2.5 : Fe/Co (wt%) on
USY Zeolite 30mg

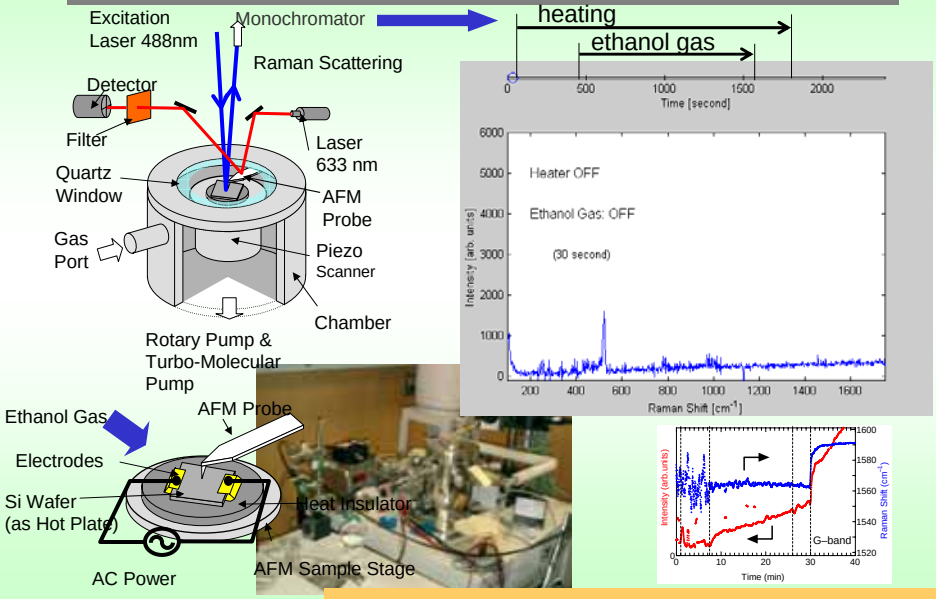


S. Maruyama et al., Chem. Phys. Lett. 360 (2002) 229.

ACCVD Experimental Apparatus

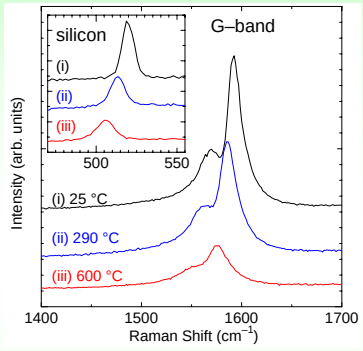


In Situ Raman During Growth

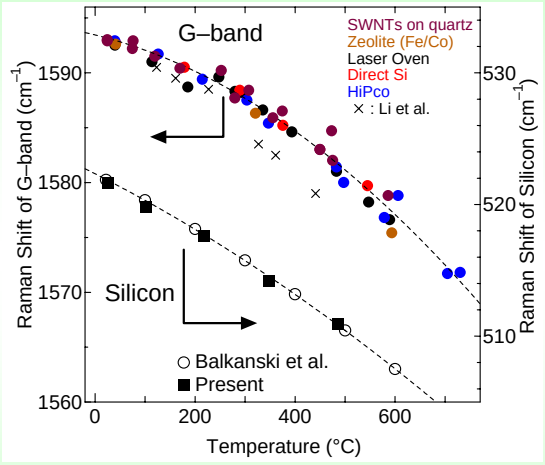


S. Chiashi et al., Chem. Phys. Lett., 386 (2004) 89.

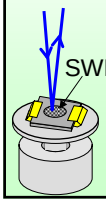
Temperature Dependence of Raman Scattering (1)



Raman scattering of SWNTs at different temperatures.



Temperature dependence of the G-band and silicon Raman peaks.



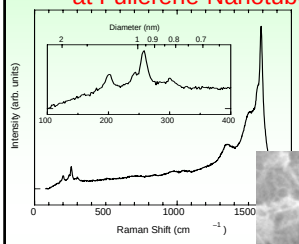
488 nm Excitation

laser power : 2 mW
laser spot : ϕ2 μm
in vacuum

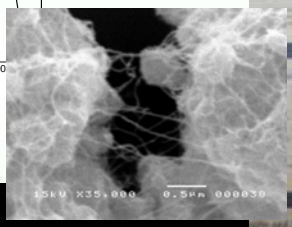
M. Balkanski et al., Phys. Rev. B (1983).
H. D. Li et al. Appl., Phys. Lett. (2000).

ACCVD is Simple!!

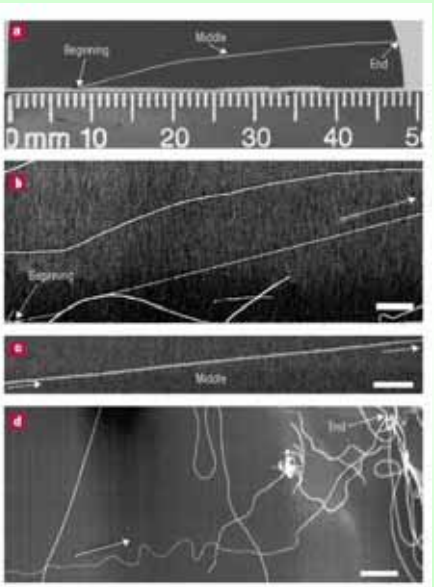
High School Students Presented
at Fullerene-Nanotubes General Symposium @ Univ. of Tokyo, July 28, 2004

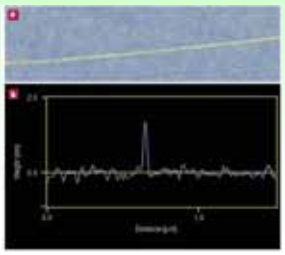


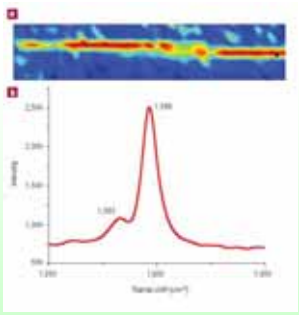
Synthesis of Single-walled Carbon Nanotubes
from Alcohol by CCVD Method
○Miki Kanao, Kieko Sawaguchi and Masaru Moriyasu
東京工業大学工学部附属工業高等学校



Ultra-Long SWNTs from Ethanol

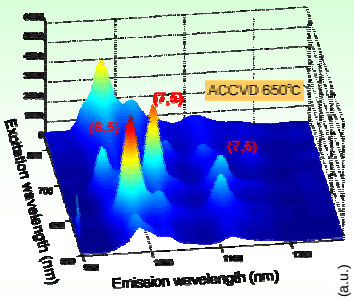


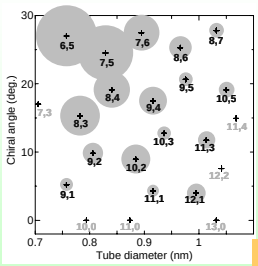




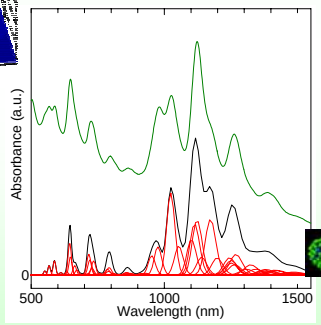
Zheng et al., Nature 2004/Los Alamos & Duke

Fluorescence Spectroscopy: Narrow Chirality Distribution

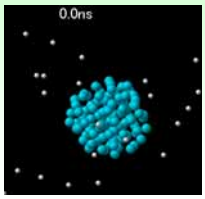




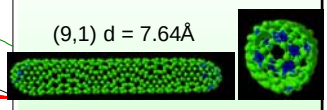
650℃



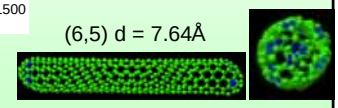
Y. Miyauchi et al., CPL 387(2004)198.



Y. Shibuta et al., CPL 382(2003)381.

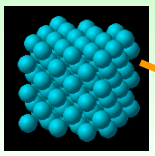


(9,1) d = 7.64Å



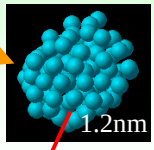
(6,5) d = 7.64Å

A MD Simulation for Formation Process of SWNTs in CCVD Method



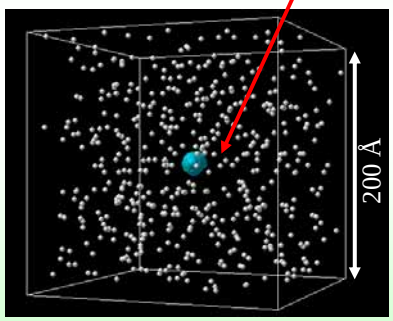
2000K

2 ns

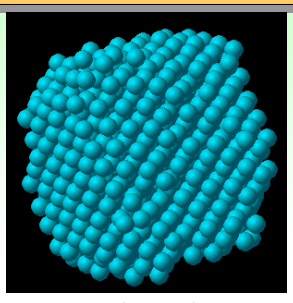


Ni_{108}: fcc

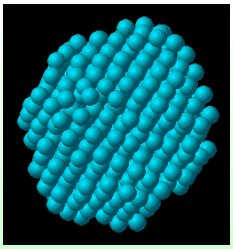
1.2nm



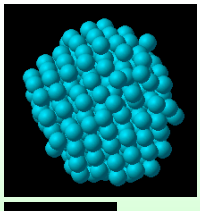
Initial position: 500 Carbon & Ni_{108} randomly distributed with random velocities



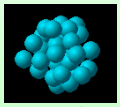
Ni_{864}(2.4nm)



Ni_{500}(2.0nm)



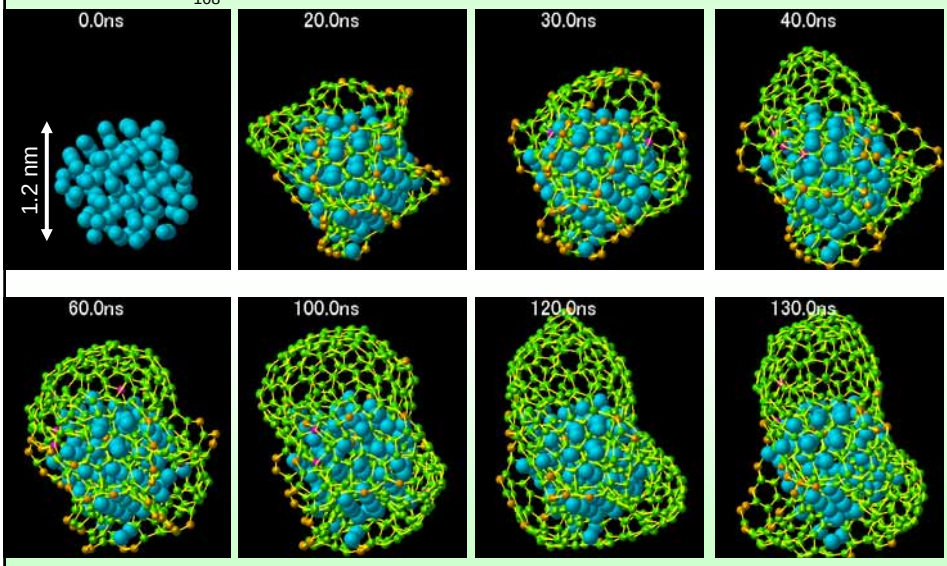
Ni_{256}(1.6nm)



Ni_{32}(0.8nm)

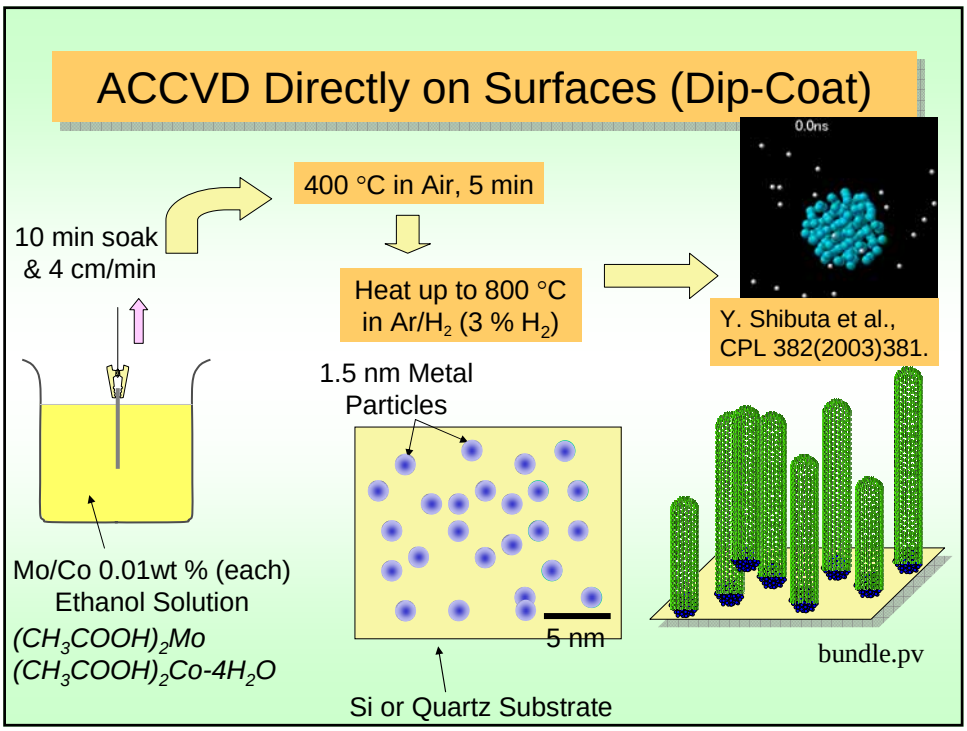
Molecular Dynamics Simulation for Mechanism

500 Carbon & Ni_{108} : 2500K

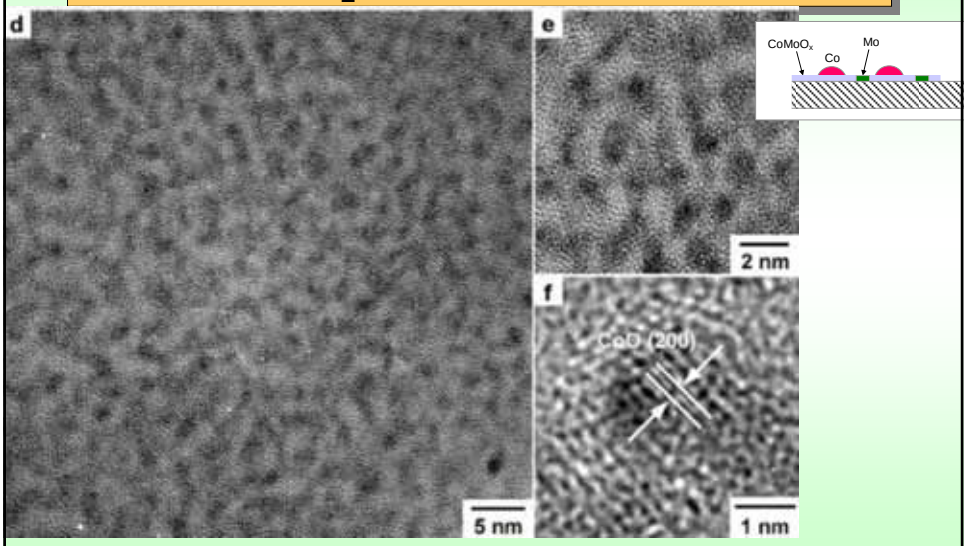


Y. Shibuta et al., CPL 382(2003)381.

ACCVD Directly on Surfaces (Dip-Coat)

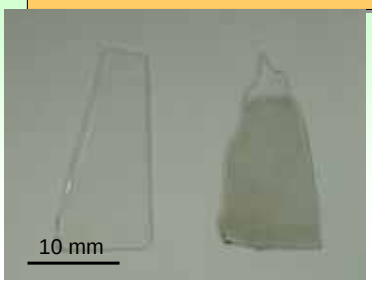


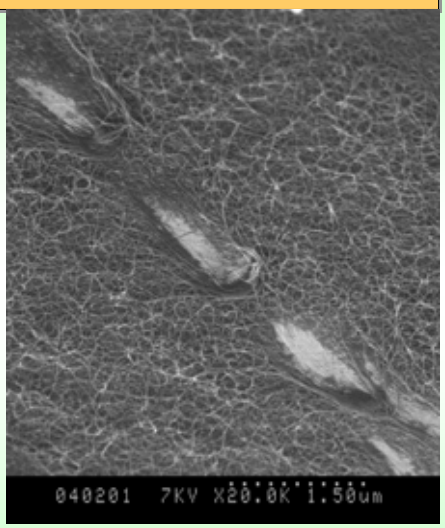
TEM images of Co-Mo catalysts on SiO_2/Si after reduction

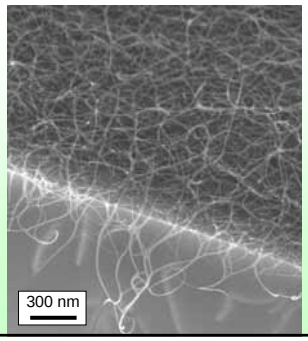


M. Hu, Y. Murakami, M. Ogura, S. Maruyama, T. Okubo, J. Catalysis 225 (2004) 230.

Direct synthesis of SWNTs on Si/quartz substrate



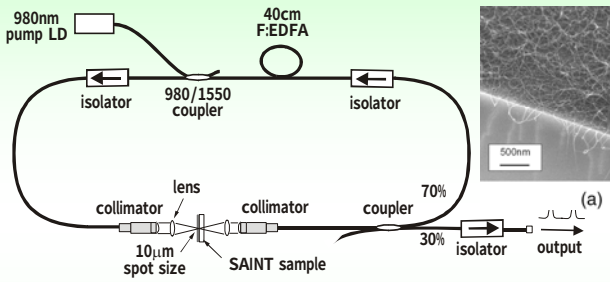


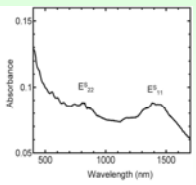


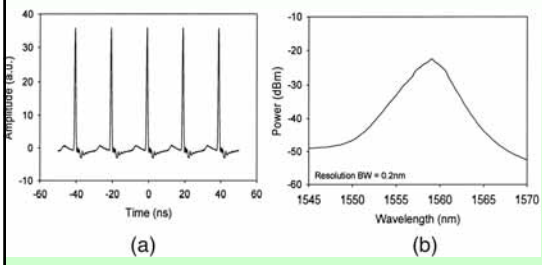
Mo/Co 0.01 wt% in EtOH
Temperature: 800 ° C, Pressure: 10 Torr
Time: 60 min, Gas used while heating: Ar/H_2 (3%)

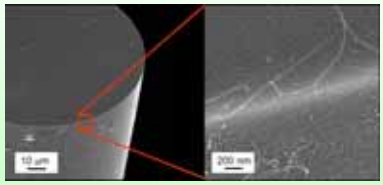
Y. Murakami et al., Chem. Phys. Lett., 377(2003)49.

Saturable Absorbers: Application to Mode-Locked Fiber Lasers







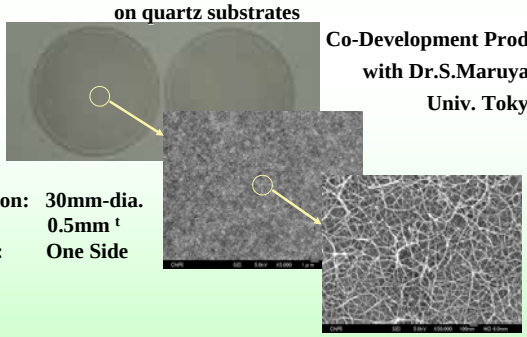


S. Yamashita, S. Maruyama, Y. Murakami, Y. Inoue, H. Yaguchi, M. Jablonski, S. Y. Set, Optics Letters, 29 (2004) 1581.

Delivery of Unique Carbon Technologies

Bussan Nanotech Research Institute, Inc.
8F Sumitomofudosan-Hamacho BDG.,
3-42-3, Nihonbashi Hamacho, Chuo-ku Tokyo, 103-0007 Japan
Contact ;
M.KATO, K.AOKI cnri@xnri.com TEL 03-5645-5572

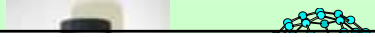
Single-Walled Carbon Nano Tubes, directly grown on quartz substrates



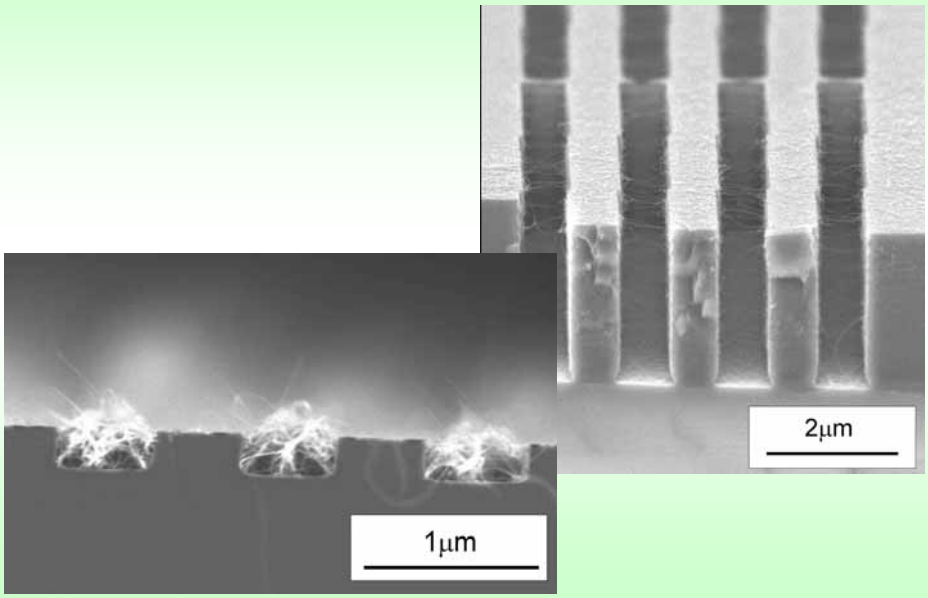
Co-Development Product with Dr.S.Maruyama, Univ. Tokyo

Dimension: 30mm-dia. 0.5mm t
Growth: One Side

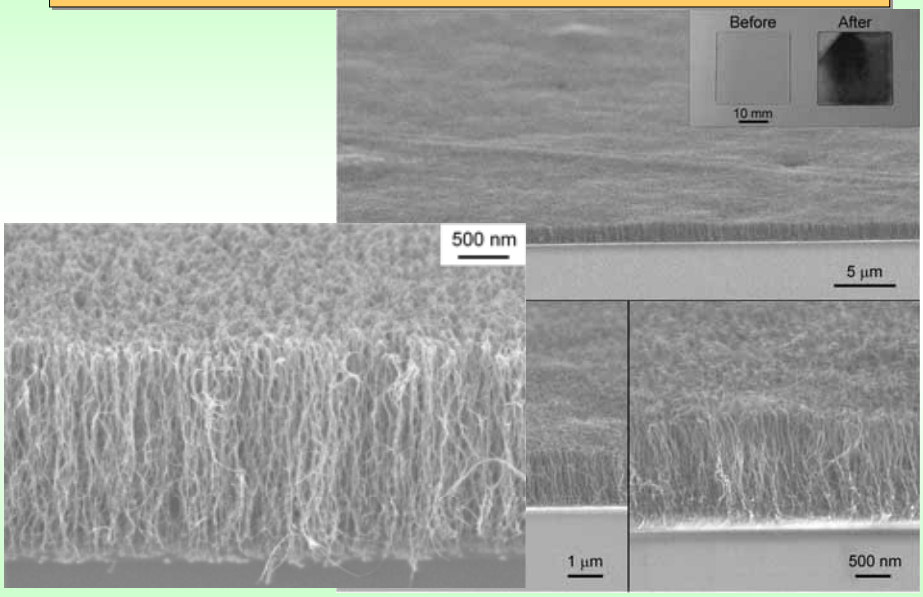
Endohedral MetalloFullerenes, La@C82



SWNTs in a Groove

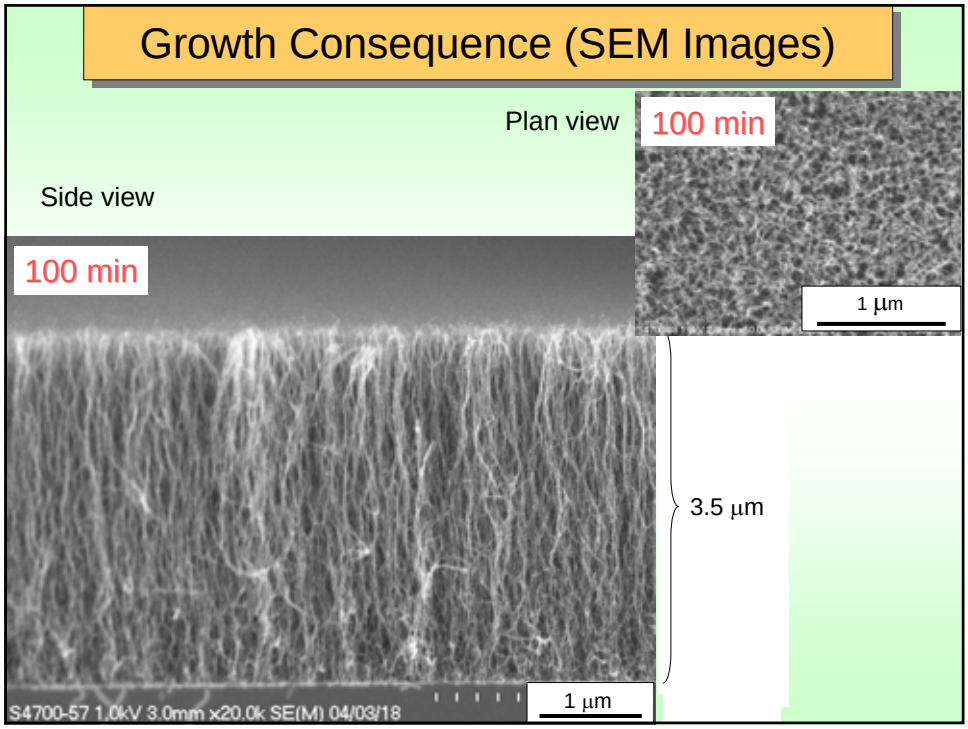


Vertically Aligned SWNTs on Quartz Substrate

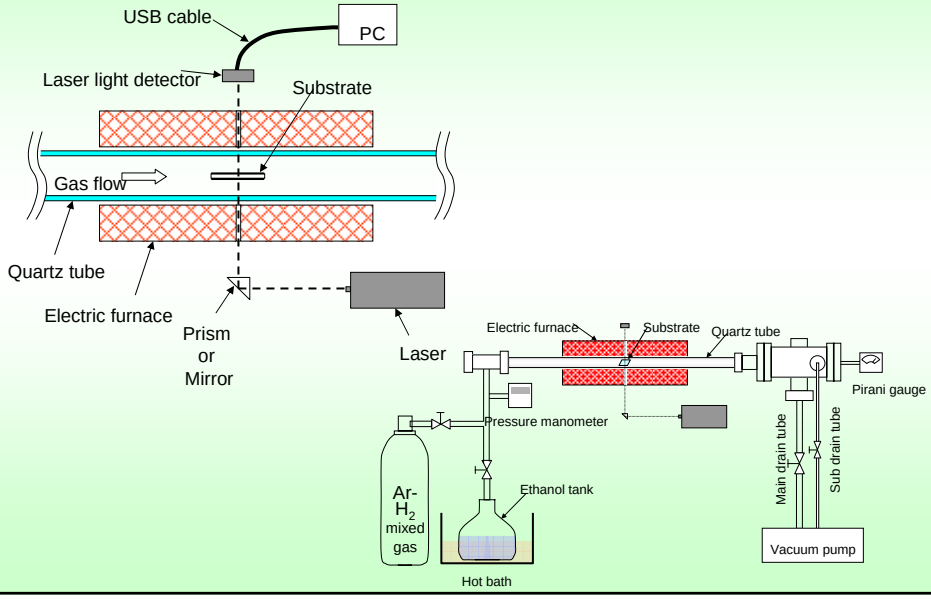


Y. Murakami, S. Chiashi, Y. Miyauchi, M. Hu, M. Ogura, T. Okubo, S. Maruyama, Chem. Phys. Lett. 385 (2004) 298

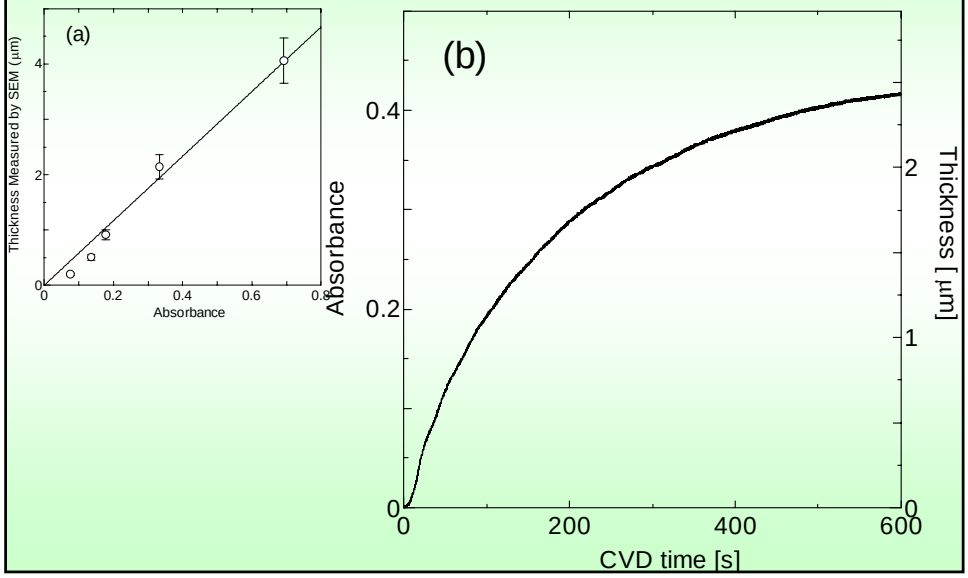
Growth Consequence (SEM Images)



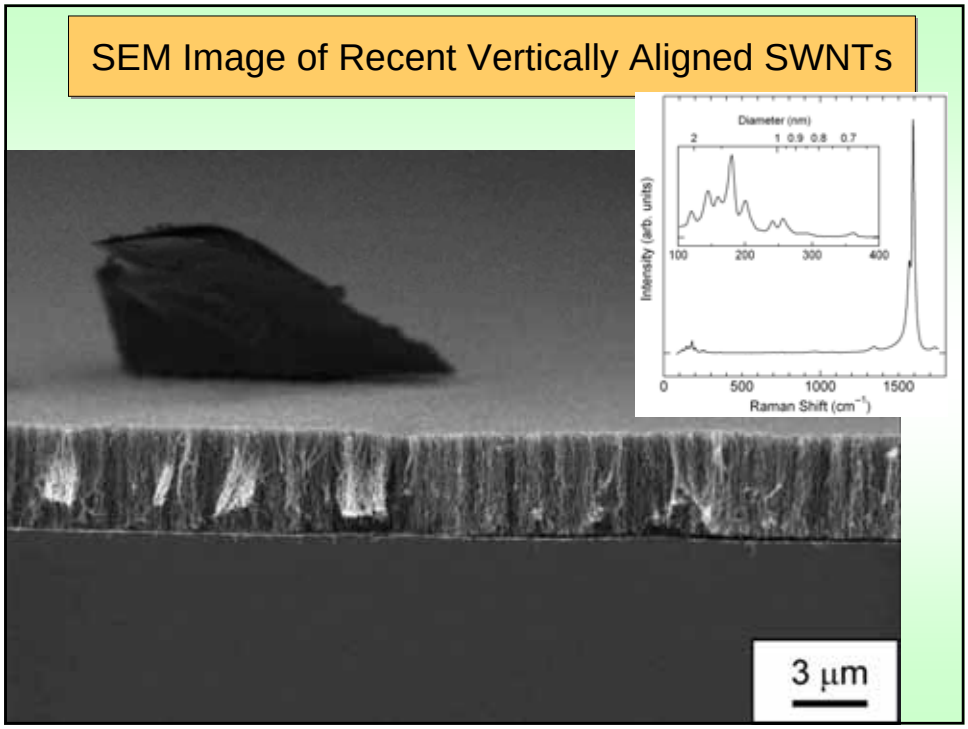
In-situ Measurement of Film Thickness



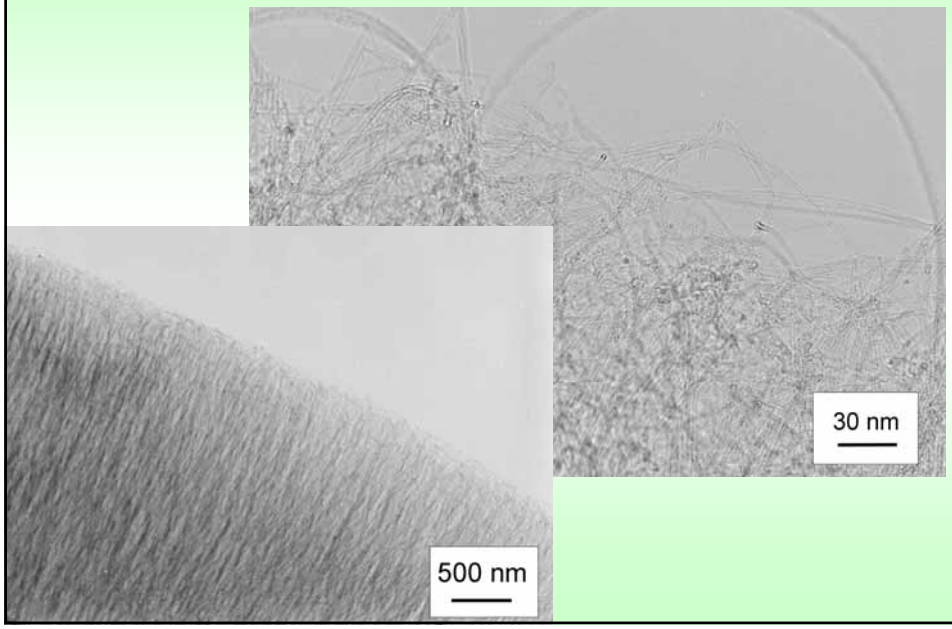
In-situ Measurement of Film Thickness



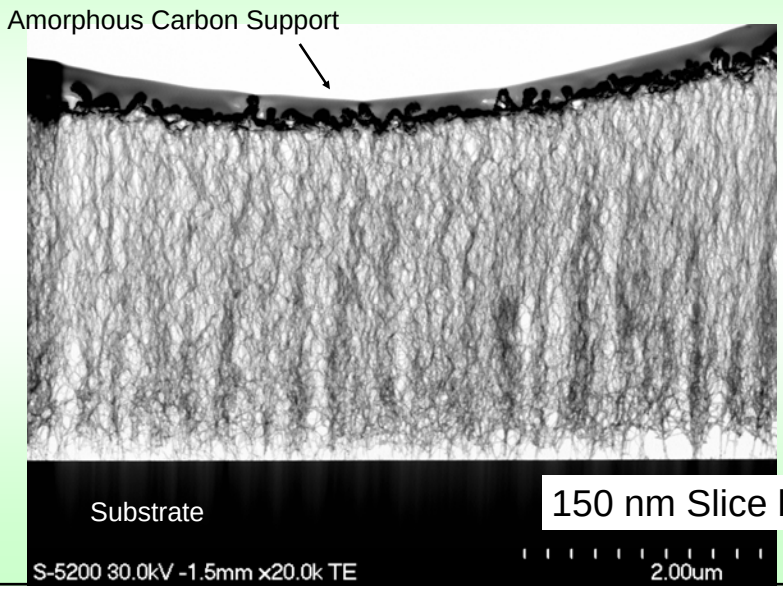
SEM Image of Recent Vertically Aligned SWNTs



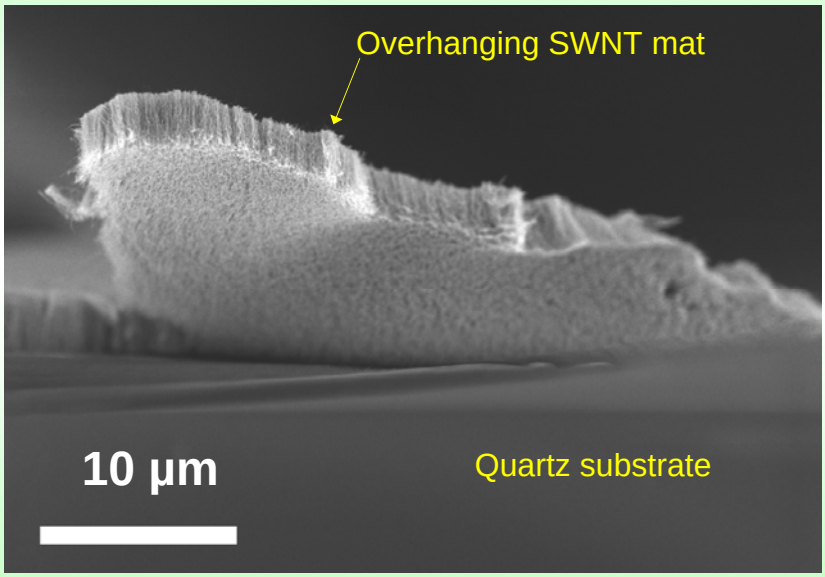
TEM Image of ‘As-Grown’ Aligned SWNTs



STEM Image of Vertically Aligned SWNTs

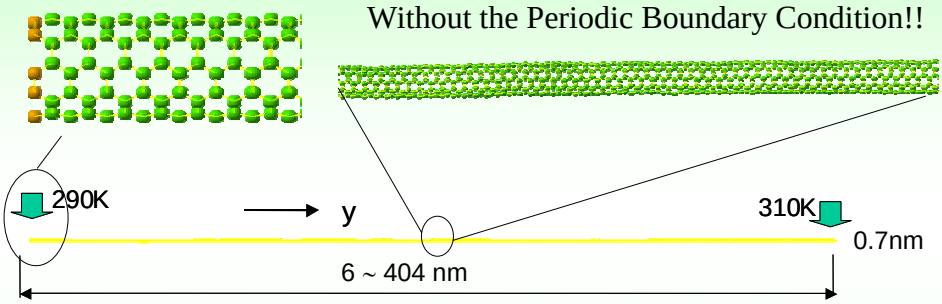


Free Standing Vertically Aligned SWNT Mat



Heat Transfer Problems with Carbon Nanotubes

MD Simulation Technique



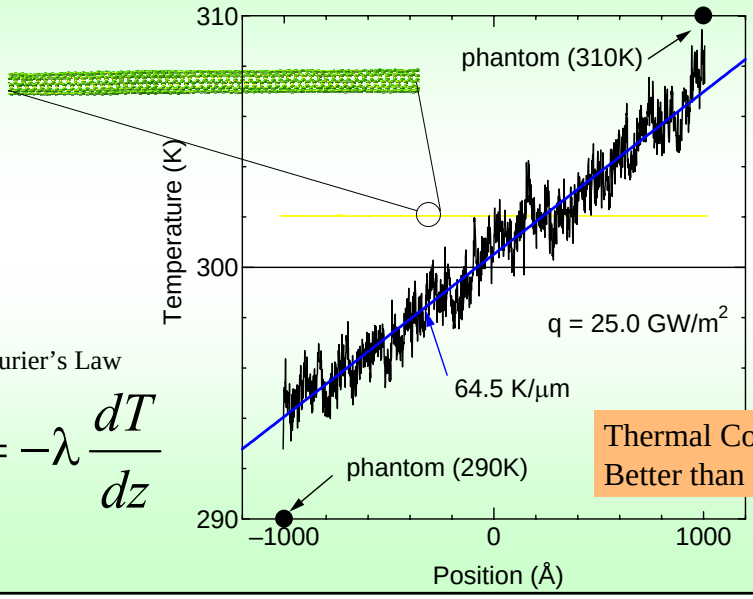
Temperature Control by Phantom Technique

$$m\ddot{\mathbf{x}} = \mathbf{f}_{Pot} + \mathbf{f}_{Rand}(\sigma) - \alpha\dot{\mathbf{x}}$$

$$\sigma = \sqrt{2\alpha k_B T_C / \Delta t_S}, \quad \alpha = m\frac{\pi}{6}\omega_D, \quad \omega_D = k_B\theta_D / \hbar$$

$$\theta_D = 2500\text{K} \ \text{(Diamond)}$$

Temperature Distribution along a Nanotube

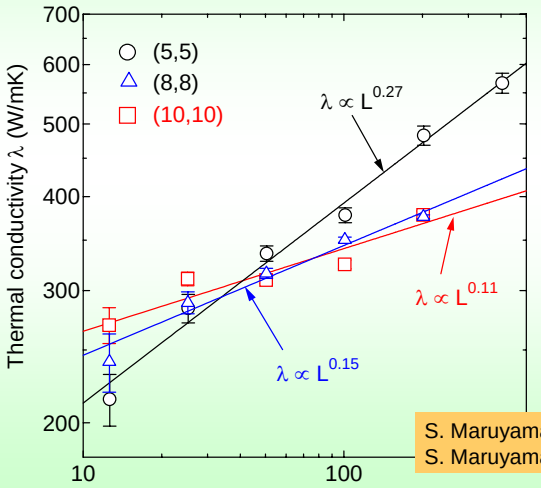


Fourier's Law

$$q = -\lambda\frac{dT}{dz}$$

Thermal Conductivity Better than Diamond?

High Thermal Conductivity

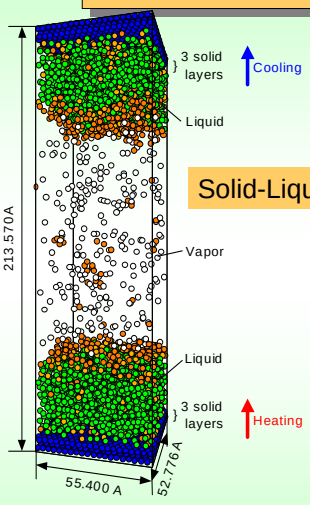


Thermal Conductivity
Higher than Diamond?

Phonon Transport

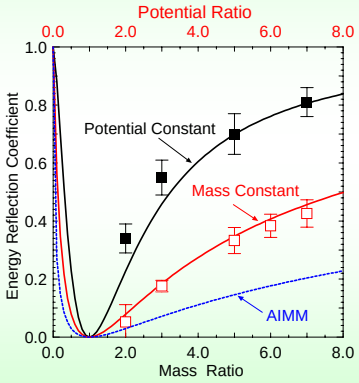
S. Maruyama, Physica B 323 (2002) 193.
S. Maruyama, Micro. Thermophys. Eng. 7 (2003) 41.

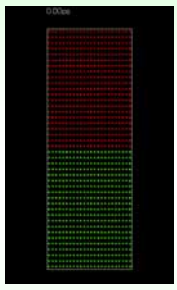
MD Studies of Thermal Boundary Resistance



Solid-Liquid

Solid-Solid



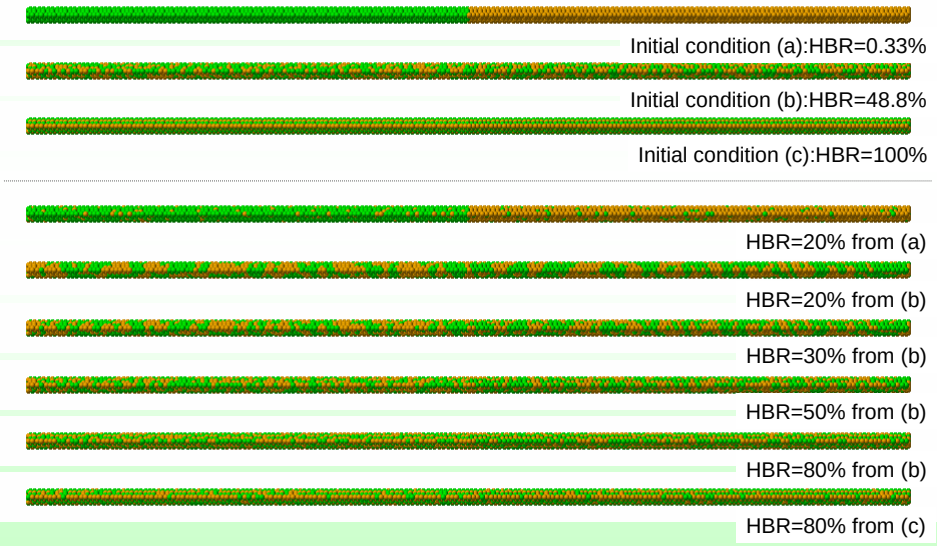


崔 淳豪

S. Maruyama, T. Kimura,
Therm. Sci. Eng., 7 (1999) 63.
K = 1-10 MW/m^{2}K

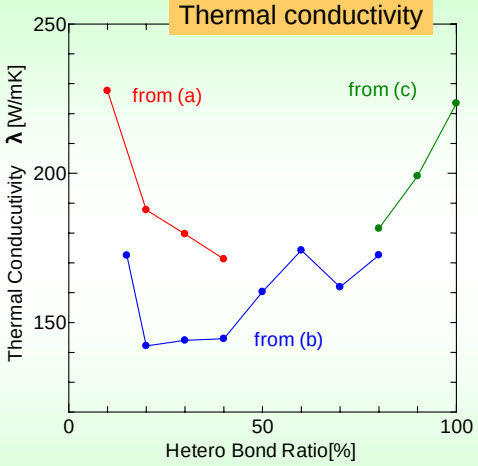
S-H. Choi, S. Maruyama, K-K Kim, J.-H. Lee
J. Kor. Phys. Soc. 44 (2004) 317.
JKPS 43 (2003) 743, JKPS in press.

SWNT with 50 % ^{13}C Isotopes

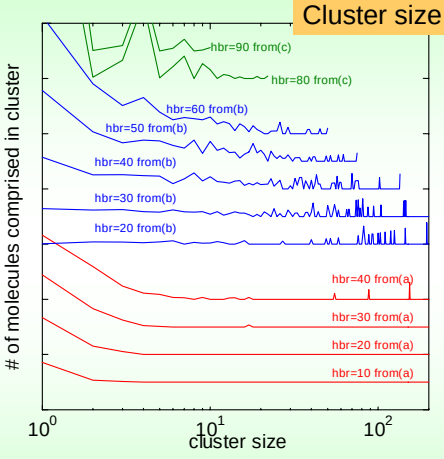


SWNT with 50 % ^{13}C Isotopes

Thermal conductivity

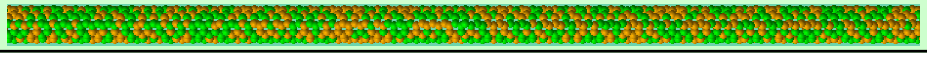


Cluster size

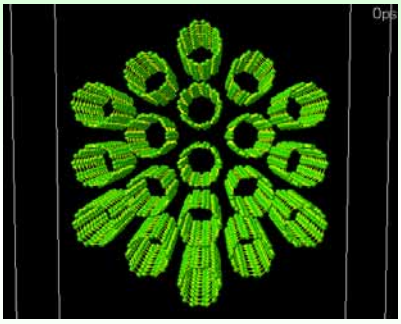


cluster size = 30~120 : dominant in decrease of thermal conductivity

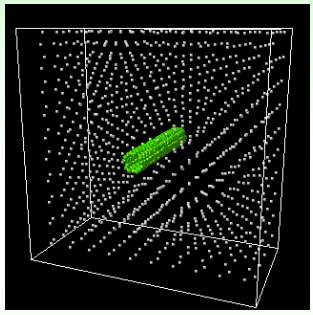
→ Estimation of frequency of phonon dominant in thermal conduction



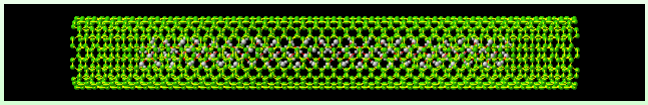
Thermal Boundary Resistances



Between SWNT and SWNT

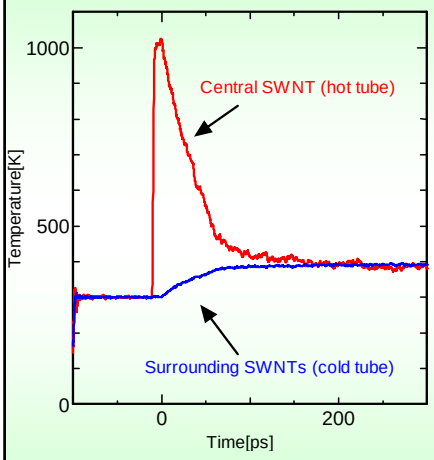


SWNT and Lennard-Jones Fluid



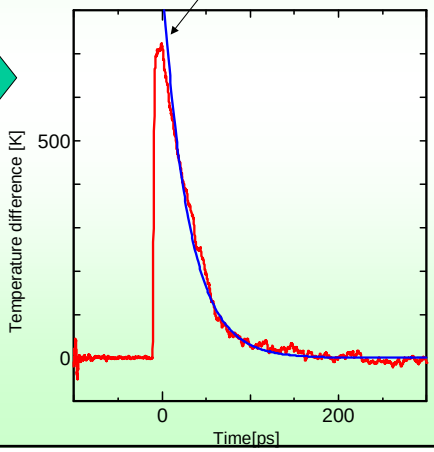
SWNT and water

Temperature Measurement



$$T_{hot} - T_{cold} = T_0 \exp\left(-\frac{t}{\tau}\right)$$

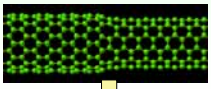
$$T_0 = 875\,[K], \quad \tau = 29.7\,[ps]$$

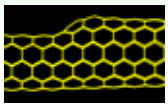


Summary of Thermal Conductance

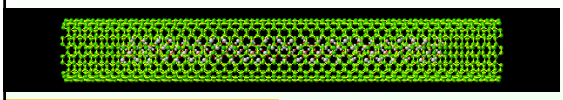
^{12}C:290K ^{13}C:310K

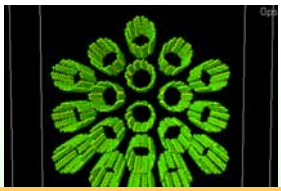
Boundary of Isotopes: K = 100,000 (MW/m^{2}K)



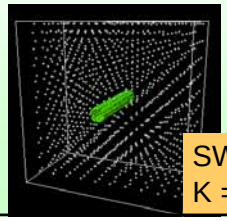


Junctions of SWNTs:
K = 14,000〜100,000 (MW/m^{2}K)





SWNT and water:
K = 8 (MW/m^{2}K)



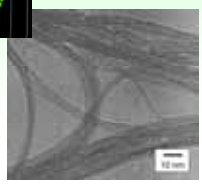
Between SWNT and SWNT :
K = 15 (MW/m^{2}K)

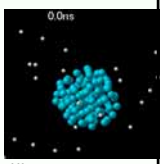
SWNT and Lennard-Jones Fluid:
K = 1 〜5 (MW/m^{2}K)

Acknowledgements (1)

MD Simulations of Heat Transfer:
Dr. Junichiro Shiomi, Mr. Yasuhiro Igarashi, Mr. Yuuki Taniguchi

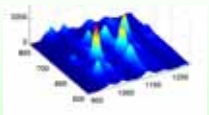
ACCVD on Zeolite:
Mr. Y. Miyauchi, Mr. S. Chiashi, Mr. Y. Murakami, Prof. M. Kohno @ Kyushu Univ.

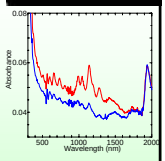




Growth Mechanism:
Dr. Y. Shibuta, Prof. S. Inoue @ Hiroshima Univ.

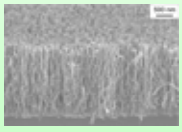
Chirality Measurements Fluorescence Spectroscopy:
Mr. Y. Miyauchi





Aligned & Isolate SWNT in Gelatin Film:
Mr. Y. Miyauchi, K. Matsuda @ Kyoto Univ., Mr. Y. Kondo, Mr. A. Saito @ Konica-Minolta

ACCVD on Flat Substrate, Vertically Aligned SWNTs
Mr. Y. Murakami, Mr. Erik Einarsson, Mr. T. Edamura
Dr. M. Hu, Prof. T. Okubo @ Univ. of Tokyo



Acknowledgements (2)

TEM: Mr. H. Tsunakawa @ Univ. of Tokyo

FE-SEM S-900: Mr. T. Sugawara @ Univ. of Tokyo (FE-SEM S-900)
FE-SEM S-4700: Mr. T. Nishii, Mr. N. Masuyama@ J-Power Co. Ltd.
FE-SEM S-5200: Mr. S. Watanabe, Ms. M. Nakagawa, Mr. R. Tamochi
@ Hitachi Science Systems

Raman Spectroscopy: Mr. M. Sunose @ Seki-Tech.

Discussions:
Prof. H. Shinohara @ Nagoya Univ.
Prof. H. Kataura, Prof. S. Suzuki, Prof. Y. Achiba @ Tokyo Metropolitan
Prof. R. E. Smalley, Prof. B. Weisman @ Rice Univ.,
Prof. R. Saito @ Tohoku Univ., Prof. S. Okada @ Tsukuba Univ.,
Dr. M. Yudasaka @ NEC

JSPS, MEXT, Toray, XNRI, J-Power, DENSO,
Konica-Minolta, Tokyo-Gas, SEL, Toso