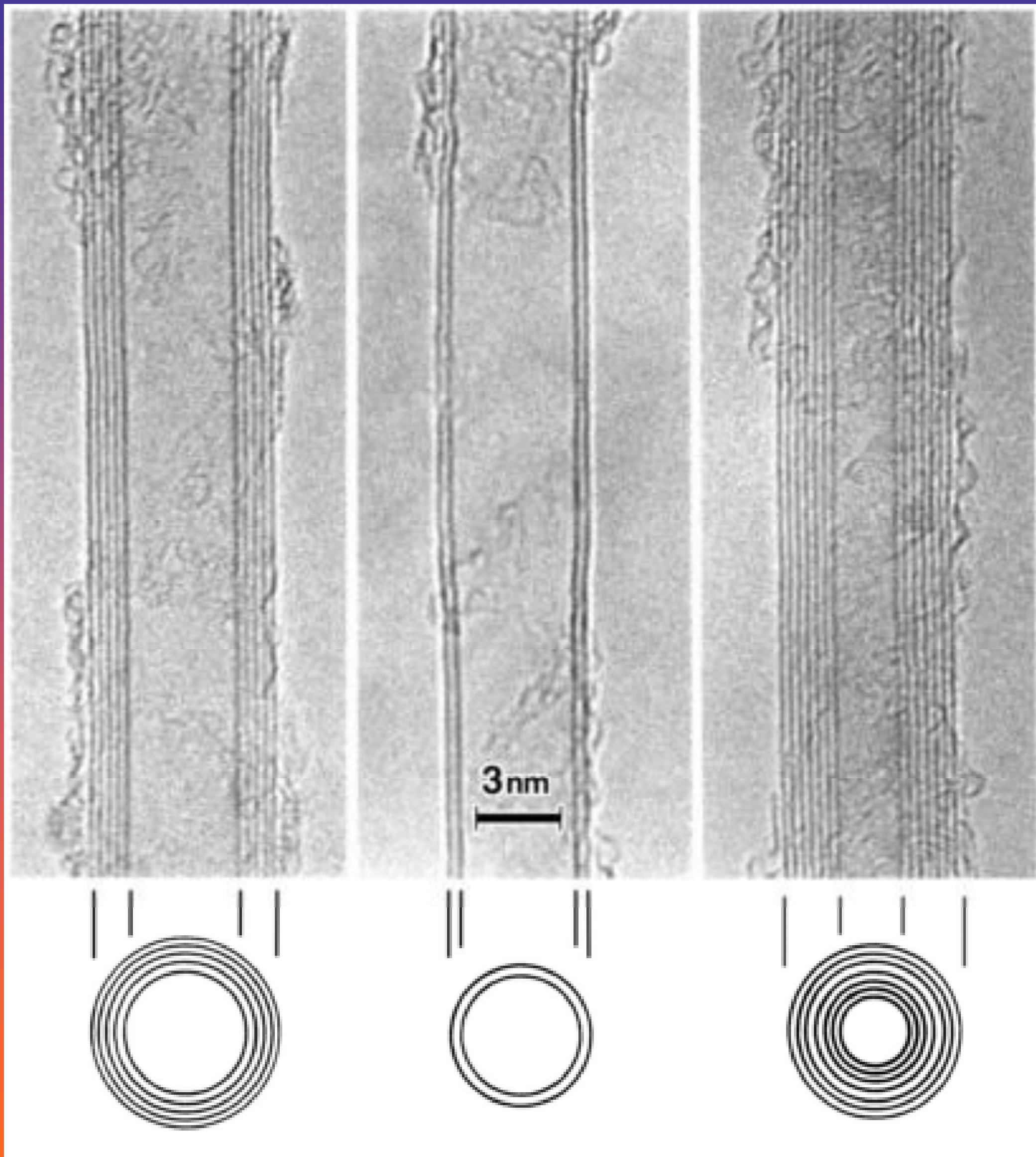
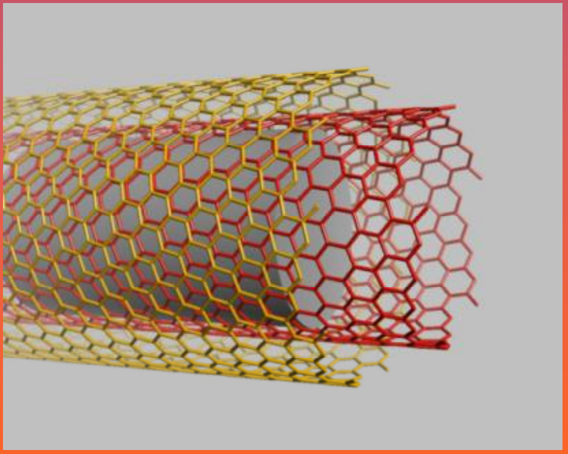
Dawn of Carbon Nanotechnology in 1991



Iijima (NEC) found these Carbon nanotubes in soot formed by arc discharge of carbon containing Fe.



Handa (NEC)

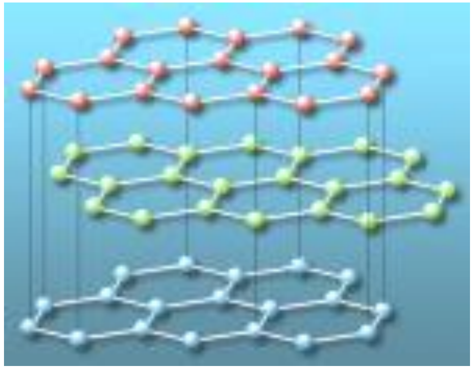
Iijima, S. *Nature 354*, 56 **1991**

Potential application of CNTs

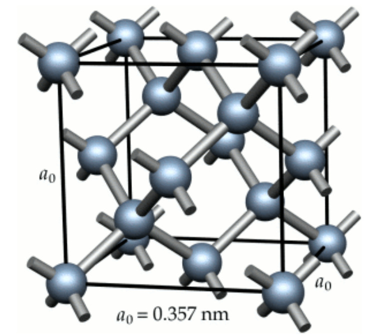
- Electronic Devices
- Large area FET
- Transparent electrically conducting films
- Coating
- Mechanical engineering fields
- Medical fields

(Robot)

Carbonaceous materials



Lanzara Research Group



John Baez's Stuff

Diamond

Graphite

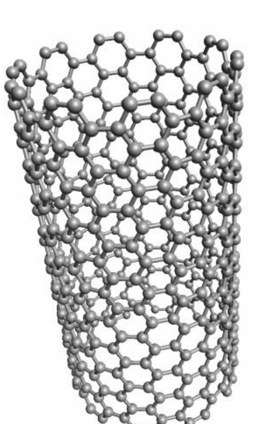
Carbon nanotube

(Single-walled, Multi-walled, Nanohorn)

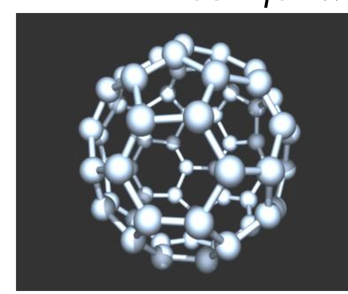
Fullerene

Others

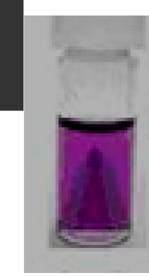
Amorphous carbon



ICSD for WWW



Yanagi et al. Diamond Related Mater. 2008



T. Kawauchi, TUT

How to make?

- Structure (C-C bonds)
- Shape
- Size
- Quality
- Quantity

Grumbach and Martin, PRB 54(1996)15730

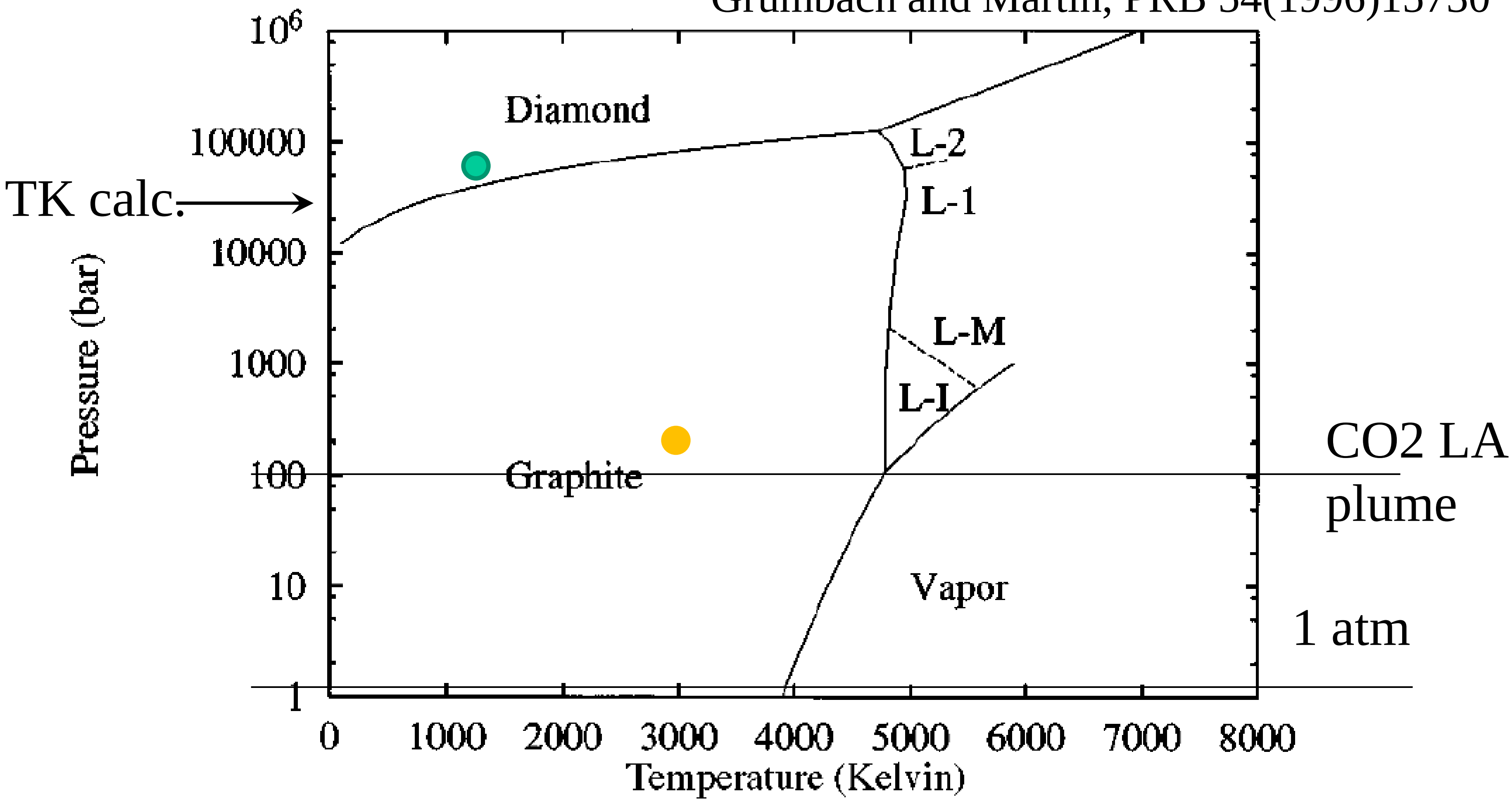
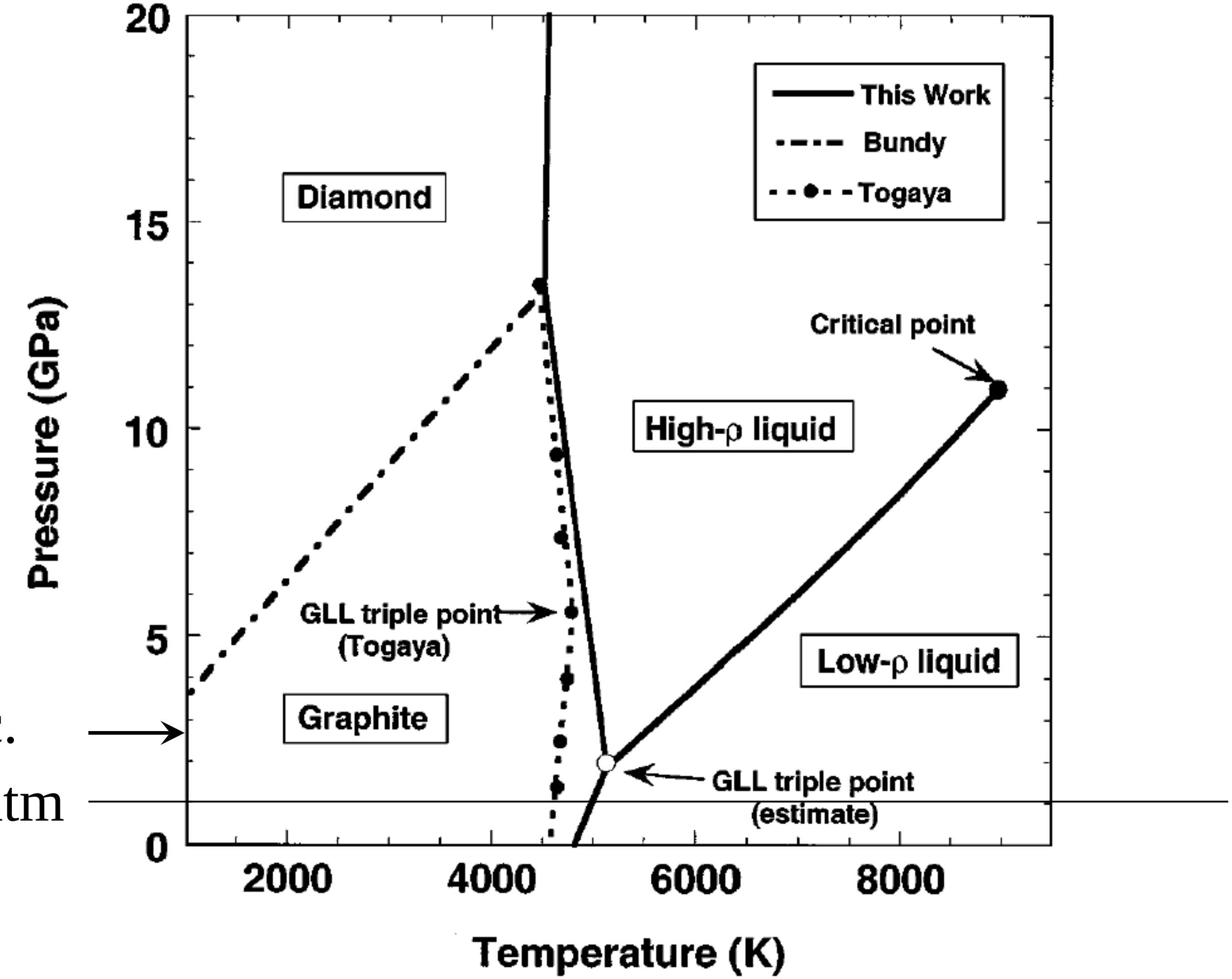


FIG. 1. Phase diagram of carbon at low pressures. Solid lines indicate phase boundaries for which some experimental evidence exists (Ref. 14). Dashed lines indicate theoretically proposed phase boundaries: liquid insulator (*L-I*) to liquid metal (*L-M*) (Ref. 15) and graphitelike liquid (*L*-1) to diamondlike liquid (*L*-2) (Ref. 16).

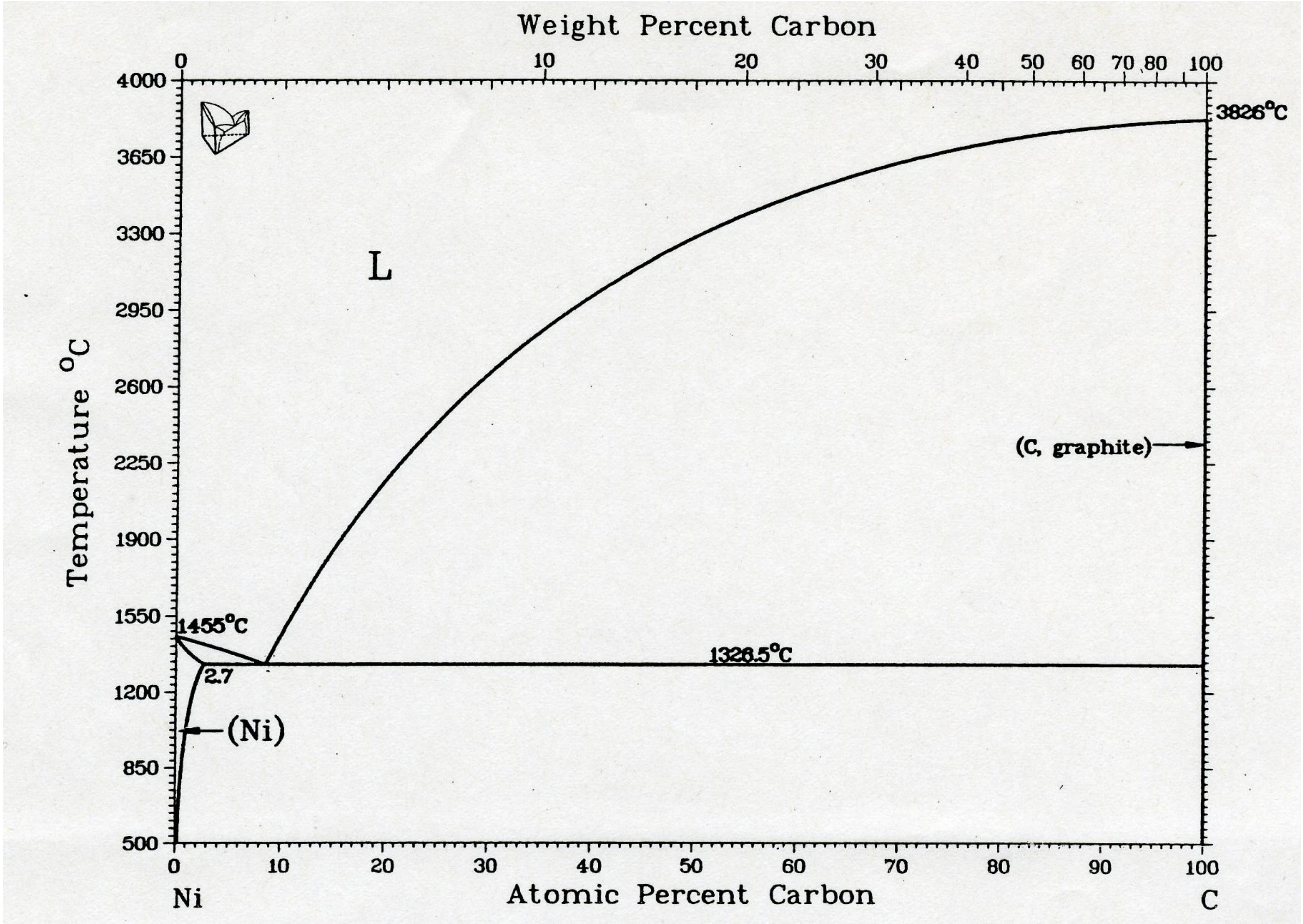
TK calc.

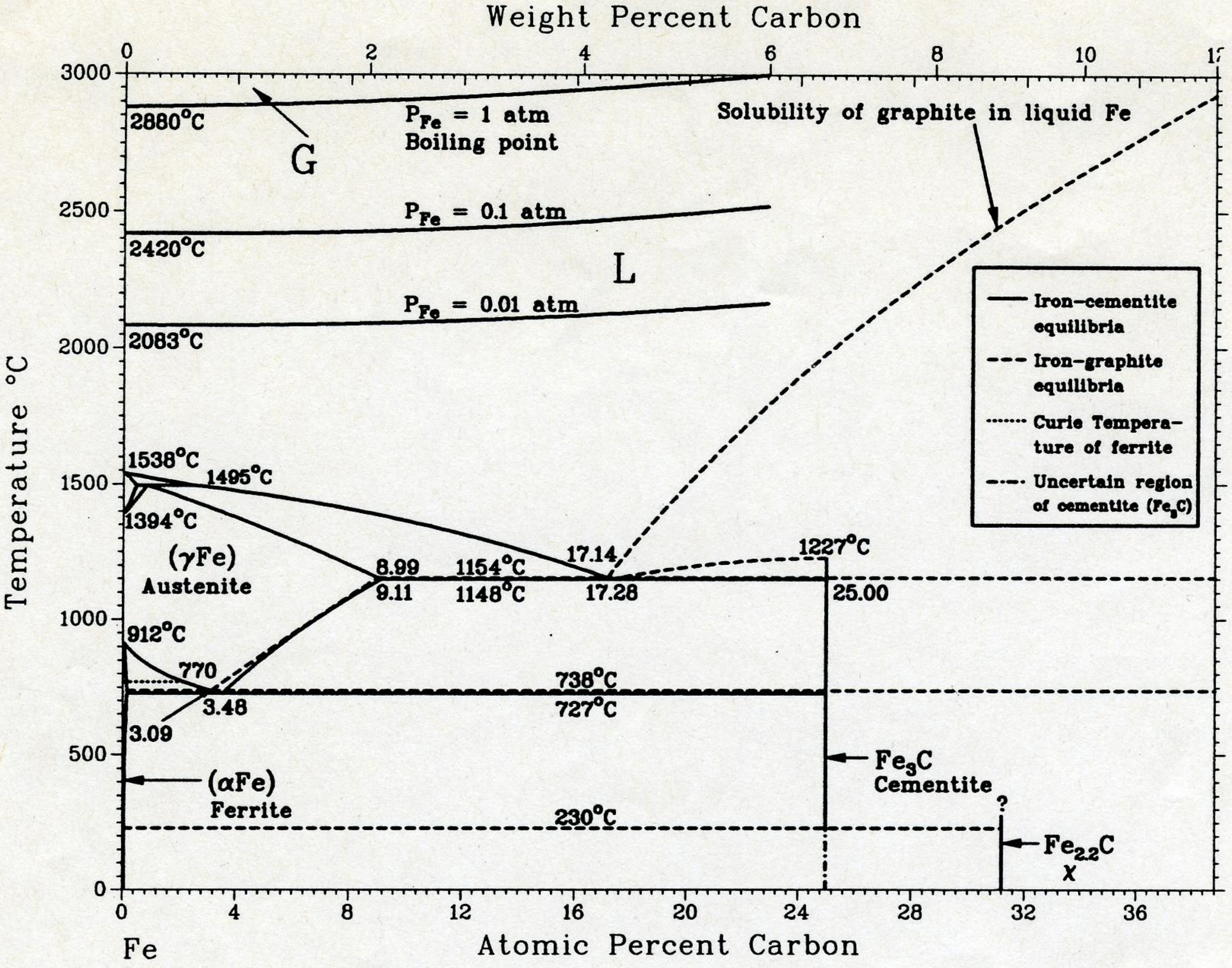
10000 atm



Glosli and Ree, *PRL* **82**(1999)4659.

Metal-Carbon Phase Diagram





Weight Percent Carbon
0
2
4
6
8
10
12
3000
2500
2000
1500
1000
500
0
2880°C
P_{Fe} = 1 atm
Boiling point
G
Solubility of graphite in liquid Fe
P_{Fe} = 0.1 atm
2420°C
L
P_{Fe} = 0.01 atm
2083°C
Iron–cementite equilibria
Iron–graphite equilibria
Curie Temperature of ferrite
Uncertain region of cementite (Fe_3C)
1538°C
1495°C
1394°C
(γFe)
Austenite
17.14
1227°C
8.99
1154°C
9.11
1148°C
17.28
25.00
912°C
770
738°C
3.48
727°C
3.09
Fe_3C
Cementite
(αFe)
Ferrite
230°C
?
$Fe_{2.2}C$
χ
0
4
8
12
16
20
24
28
32
36
Fe
Atomic Percent Carbon
Temperature °C

合成法には2種類あり、高圧（約5万気圧. 5070 bar)と高温（約1500℃）で作る高温高圧合成法と、低圧（約0.1気圧）のメタンと水素から成る原料ガスをプラズマ中で反応させ、約1000℃の基板上に堆積させる気相合成法がある。

Graphite synthesis from polyimide films

3000°C and 300 kg/cm^2 (294 bar, 290 atm, 30 MPa)

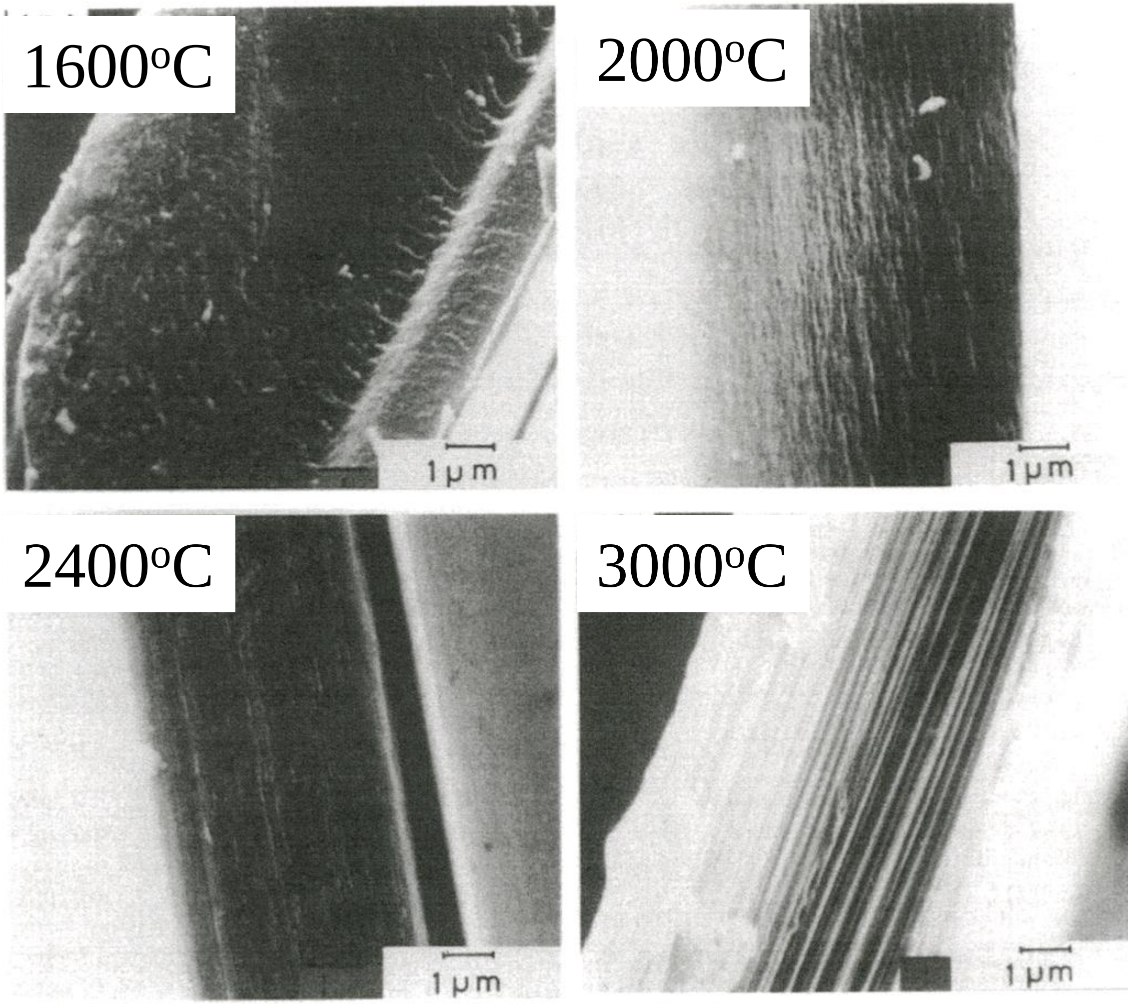
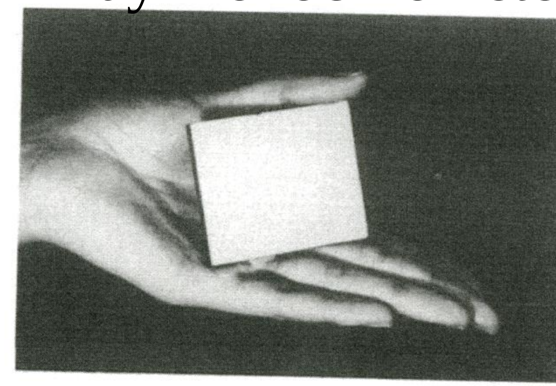
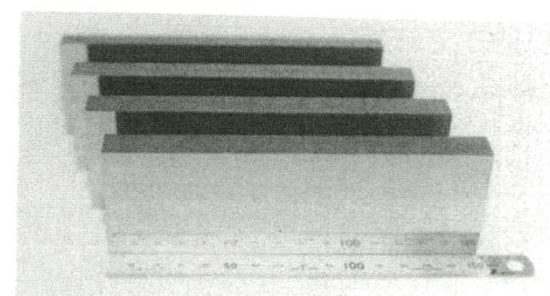


Fig. 1. Cross-sectional views of heat-treated polyimide (Kapton®) by SEM observation; (a): 1600°C, (b): 2000°C, (c): 2400°C, (d): 3000°C.

X-ray monochrometer



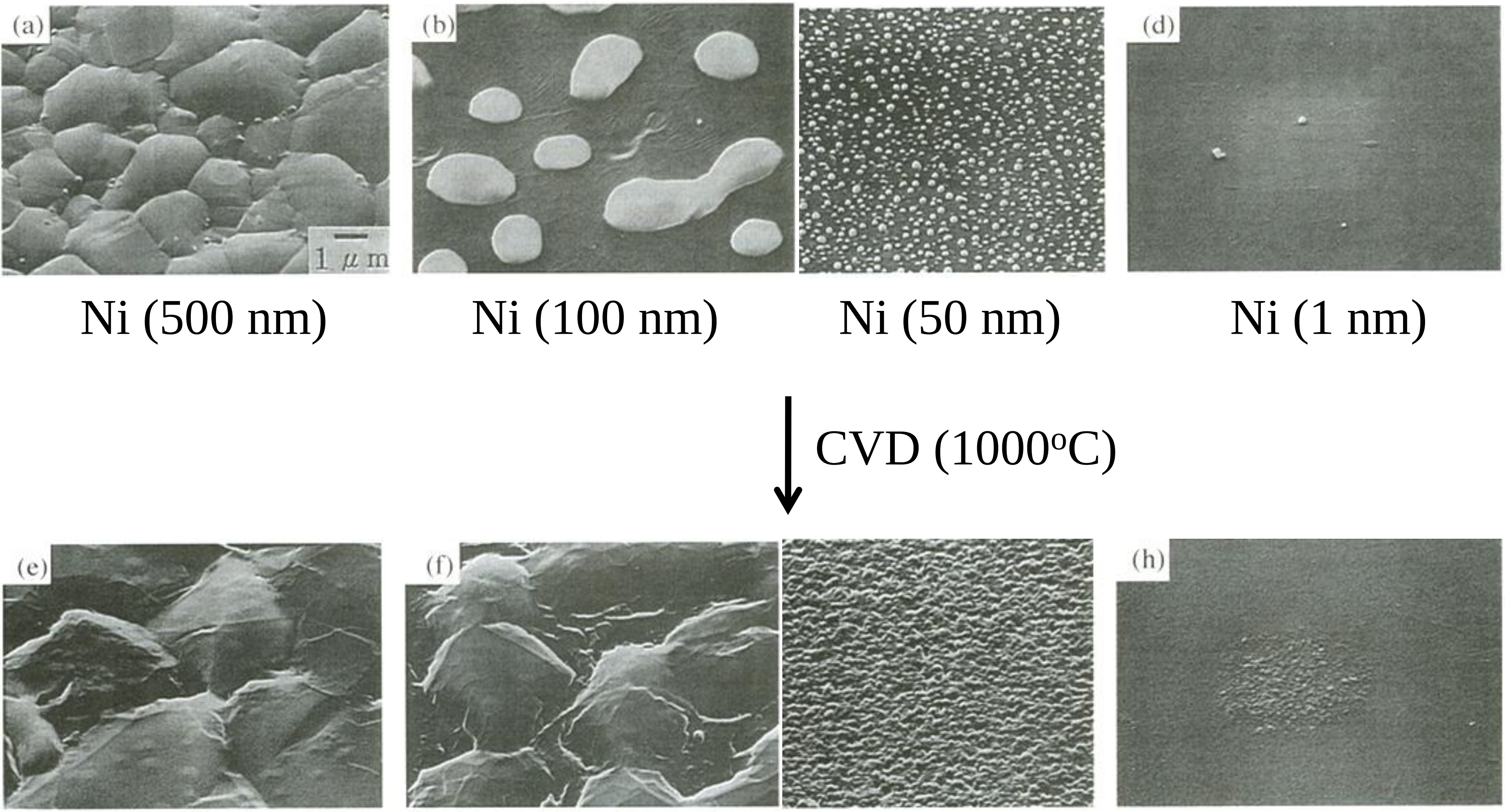
(a)



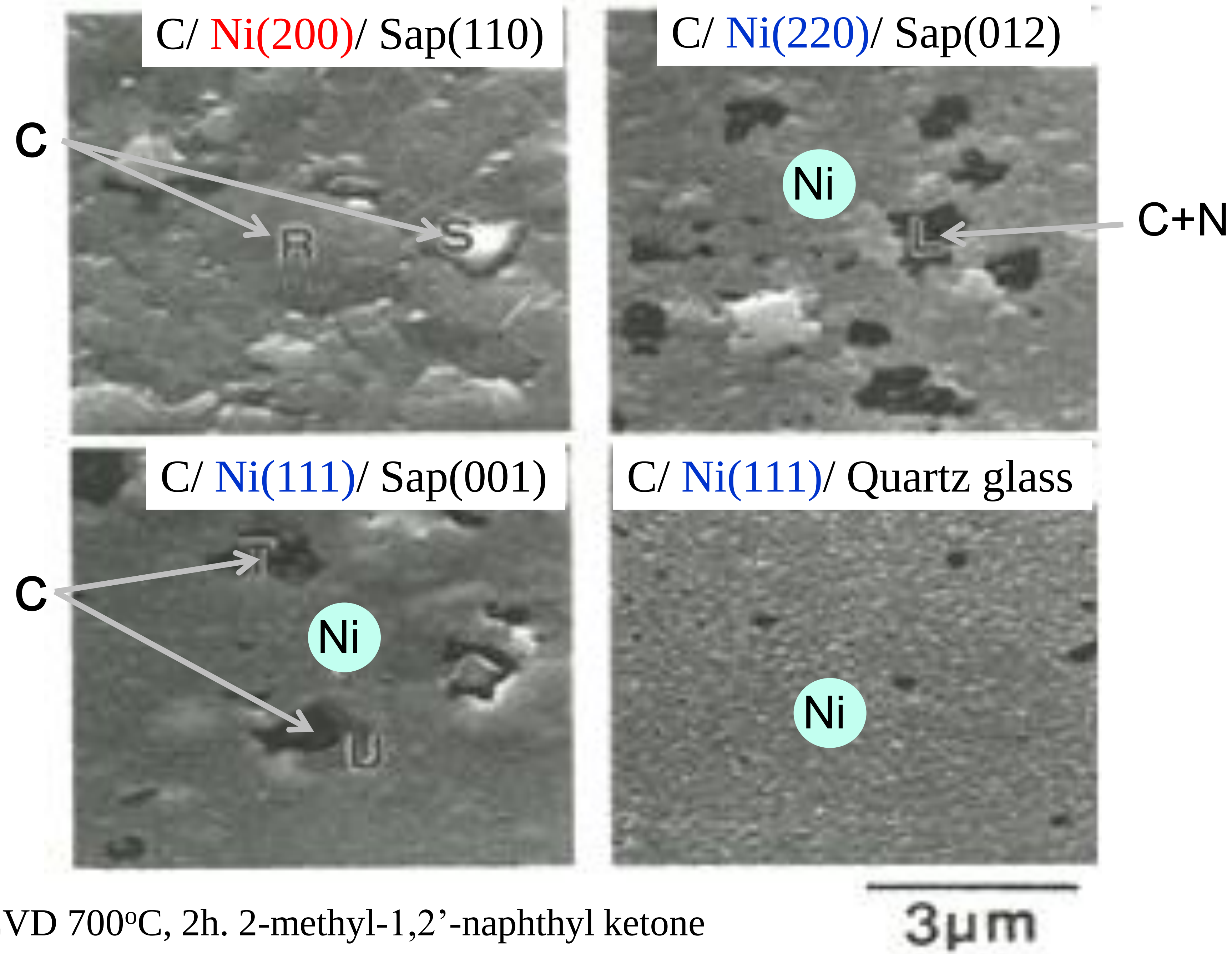
Neutron filter

Murakami et al. Carbon 1992

Graphite Thin Film Formation by CVD on Ni/Quartz glass



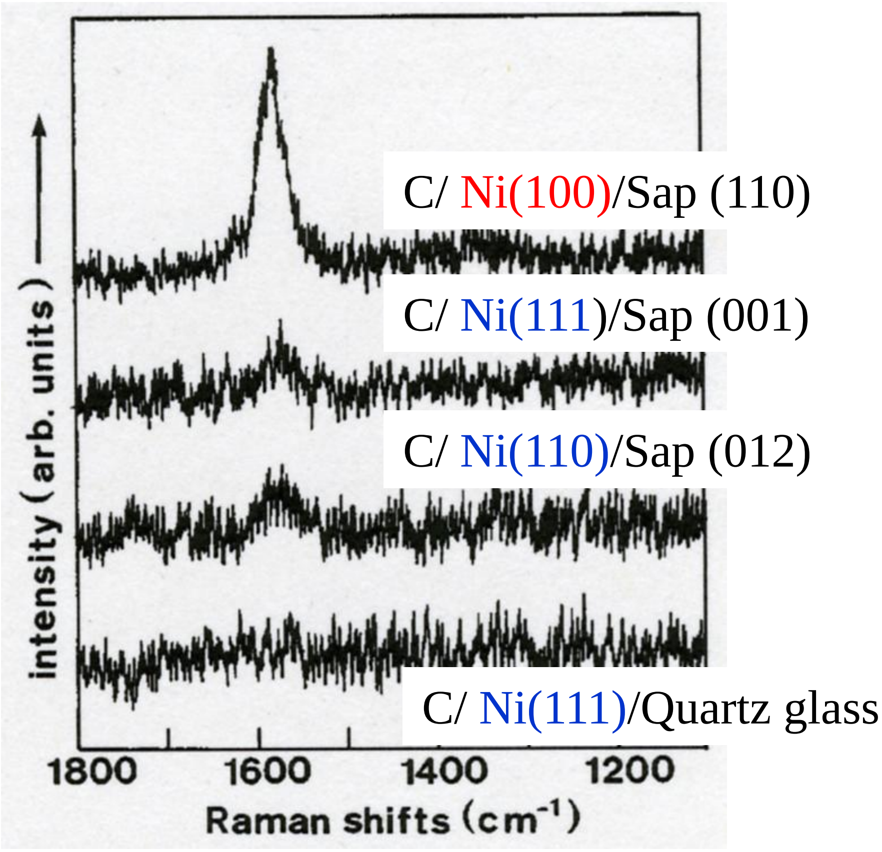
Yudasaka et al. Thin Solid Films



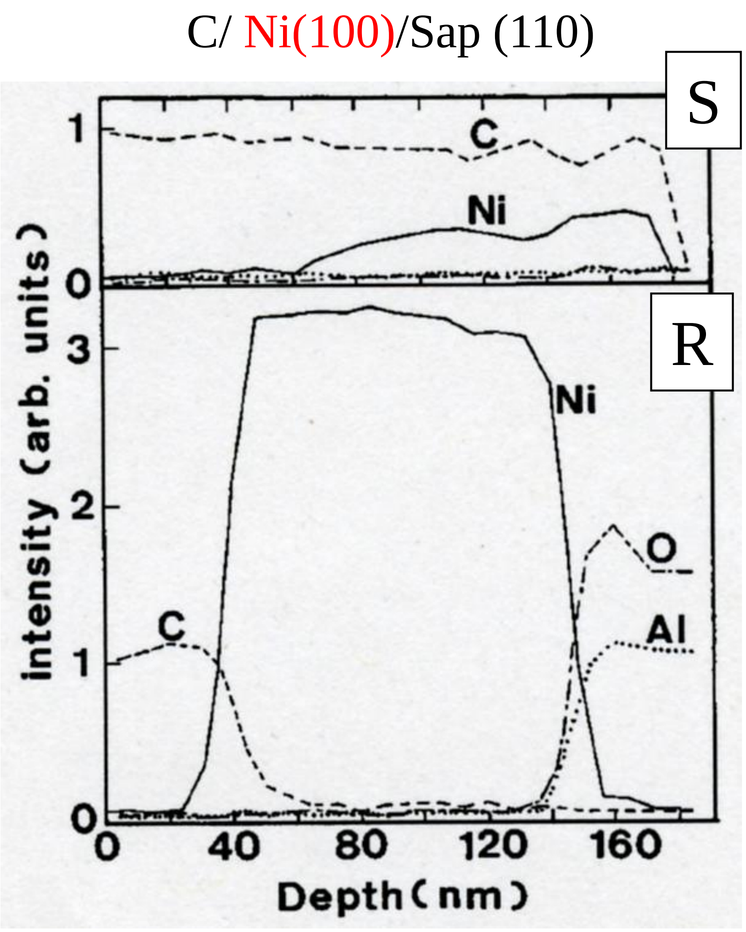
CVD 700°C, 2h. 2-methyl-1,2'-naphthyl ketone
Ni film thicknness: 50 nm

Yudasaka et al. J. Vac. Sci. Technol. A 1998.

Graphite formation on Ni(100) >> Ni(111), Ni(110)



Raman scattering spectra



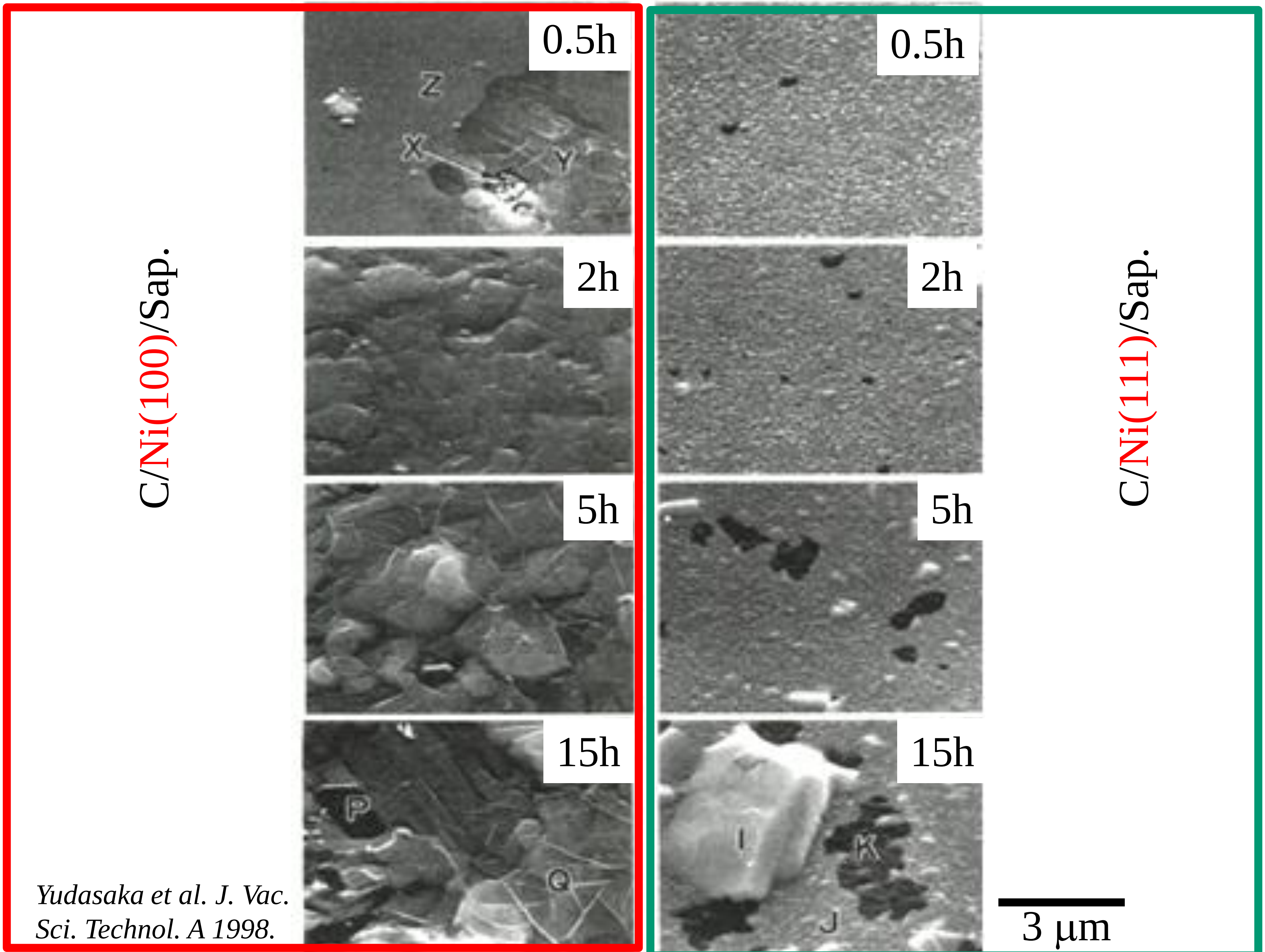
Selected Area Auger analysis
(Depth profiles of elements)

Yudasaka et al. J. Vac. Sci. Technol. A 1998.

Material name	Nickel			
Composition	Ni			
Chemical formula weight	58.69			
System	Cubic			
Temperature (ºC)	25			
a (Å), b (Å), c (Å)	3.5238(3)	3.5238(3)	3.5238(3)	
α (deg), β (deg), γ (deg)	90	90	90	
Unit cell volume (Å^3)	43.76			
Calculated density (g/cm^3)	8.91			
Z	4			
Space group	$Fm3m$ (No.225)			

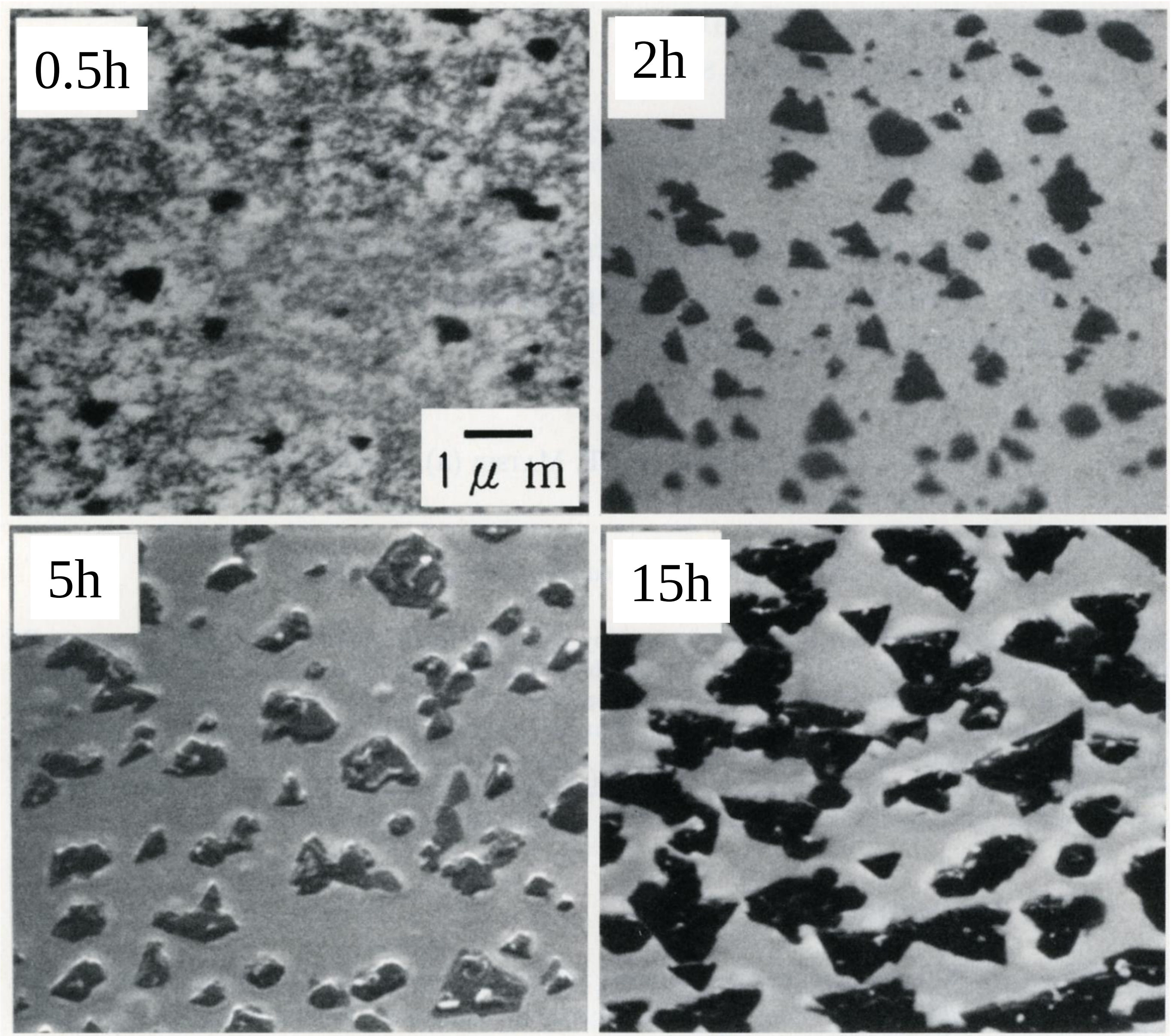
atom	site	g	x/a	y/b	z/c	B (Å^2)
Ni	4a	1	0	0	0	-

Reference: F.W. von Batchelder and R.F. Raeuchle, Acta Crystallographica, **7**, 464 (1954).



Yudasaka et al. J. Vac. Sci. Technol. A 1998.

Graphite/Pt(111)/Sapphire(110)



CVD 900^{o}C,
Pt 50 nm
Pt(111)
Sapphire (110)

Yudsasaka et a l. phys. stat. sol. (a) **156**, 107 (1996)

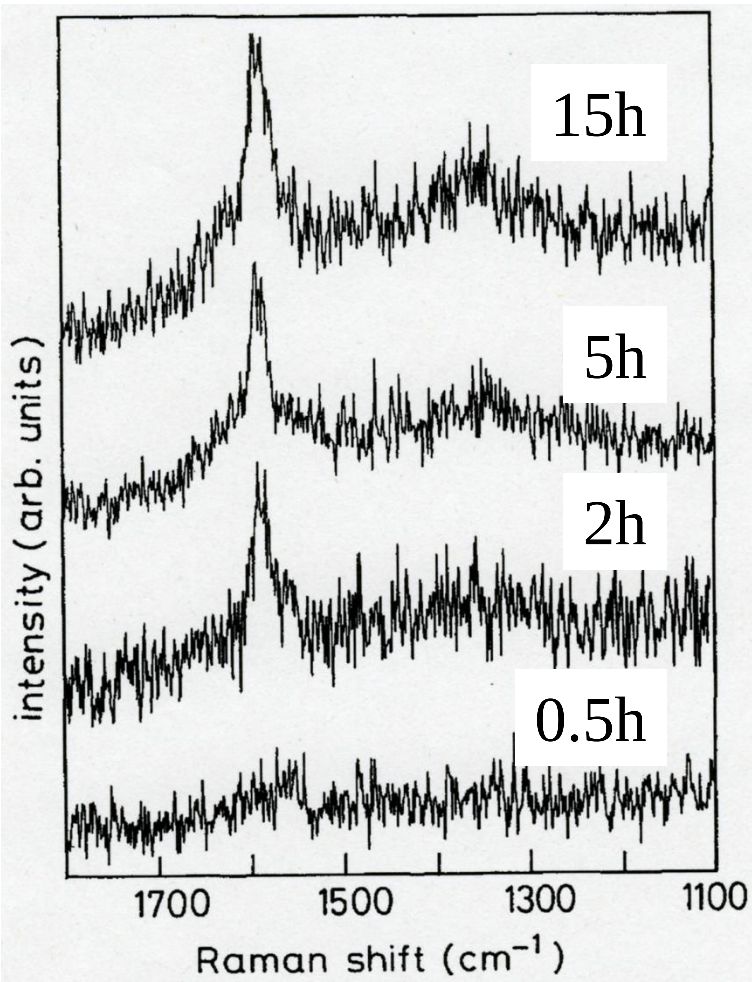
time (h)	0.5	2	5	15	2 + 18
d_{002} (nm)	(0.3373)	0.3356	0.3352	0.3353	0.3358
Δ_{002} (^{o})		0.37	0.26	0.18	0.25
δ_{222} (^{o})	(0.33)	0.27	0.25	0.28	0.18
d_{222} (nm)	0.1130	0.1129	0.1127	0.1127	0.1131
Δ_{222} (^{o})	0.20	0.20	0.22	0.19	0.22
δ_{222} (^{o})	0.11	0.14	0.12	0.13	0.14

Pt film: d_{222}=0.1129 nm → 0.3387 nm

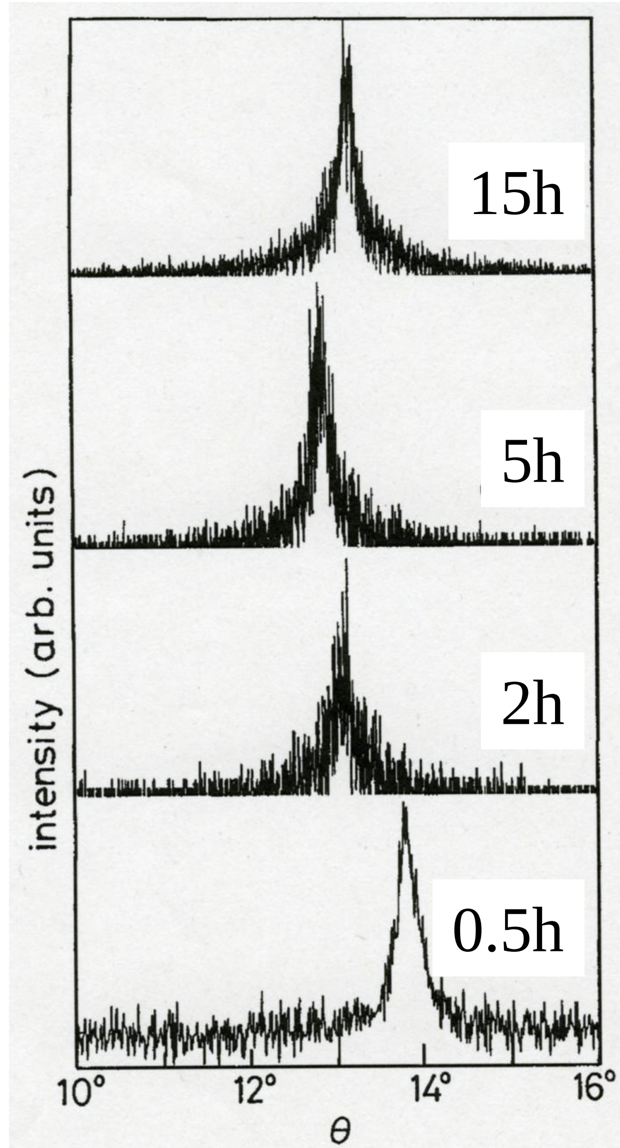
Pt crystal: d_{222}=0.11325 nm → 0.33975 nm

Material name			**Platinum**			
Composition			Pt			
Chemical formula weight			195.08			
System			Cubic			
Temperature (ºC)			18			
a (Å), *b* (Å), *c* (Å)			3.924	3.924	3.924	
α (deg), *β* (deg), *γ* (deg)			90	90	90	
Unit cell volume (Å^3)			60.4			
Calculated density (g/cm^3)			21.5			
Z			4			
Space group			*Fm*3*m* (No.225)			
atom	site	g	*x*/*a*	*y*/*b*	*z*/*c*	*B* (Å^2)
Pt	4*a*	1	0	0	0	-

Graphite/Pt(111)/Sapphire(110)



Raman spectra

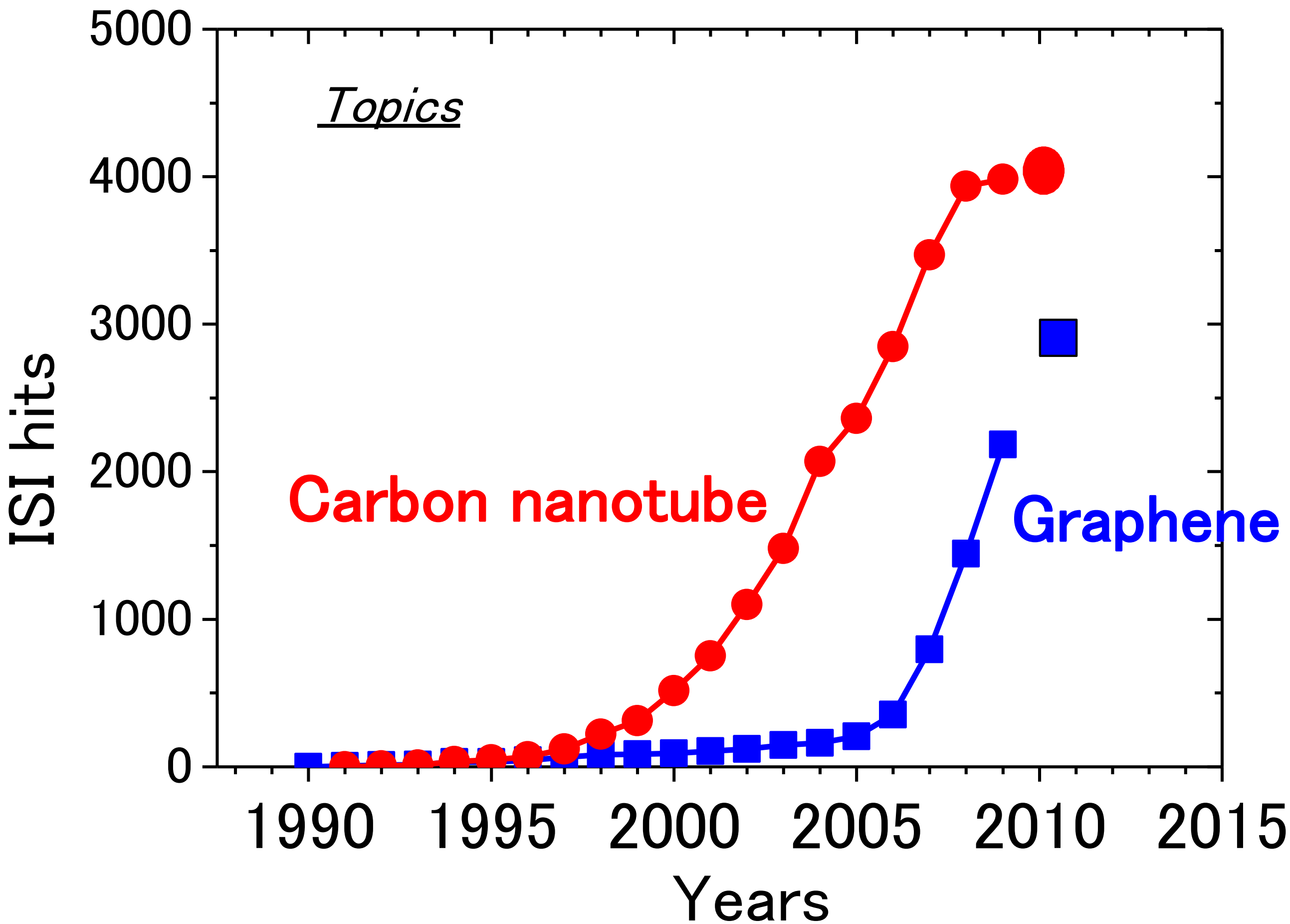


X-ray diffdaction rocking curves

Yudsasaka et a l. phys. stat. sol. (a) **156**, 107 (1996)

Studies on Graphene: Quickly Increasing

2010 (July) 1446
2009 2185
2008 1444
2007 796
2006 352
2005 205
2004 161
2003 147
2002 119
2001 106
2009 90
1999 85
1998 83
1997 64
1996 44
1995 31
1994 30
1993 15
1992 12
1991 5

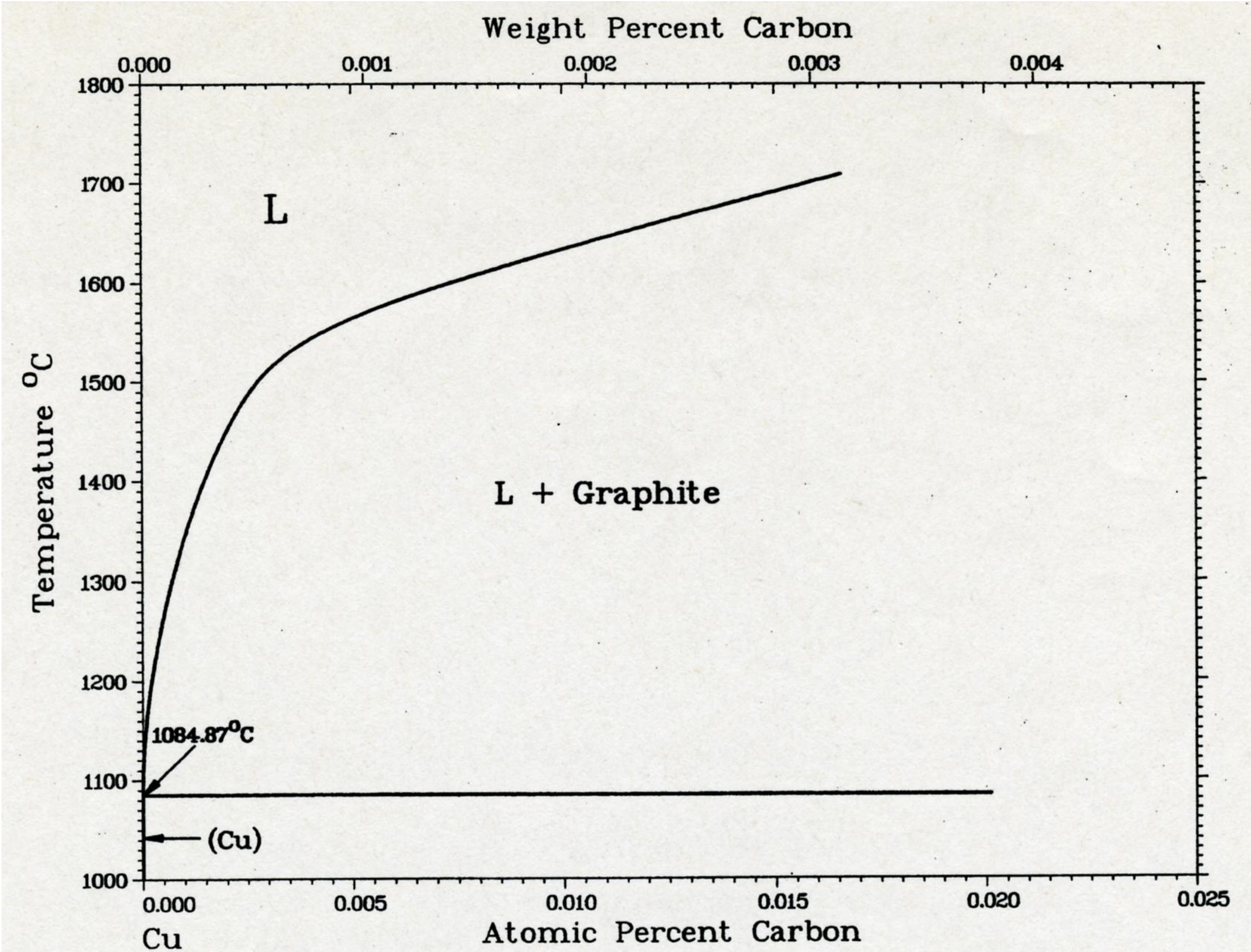


How to obtain graphenes?

~2005 Peeling

Recently   CVD on Cu

Cu-C Phase diagram

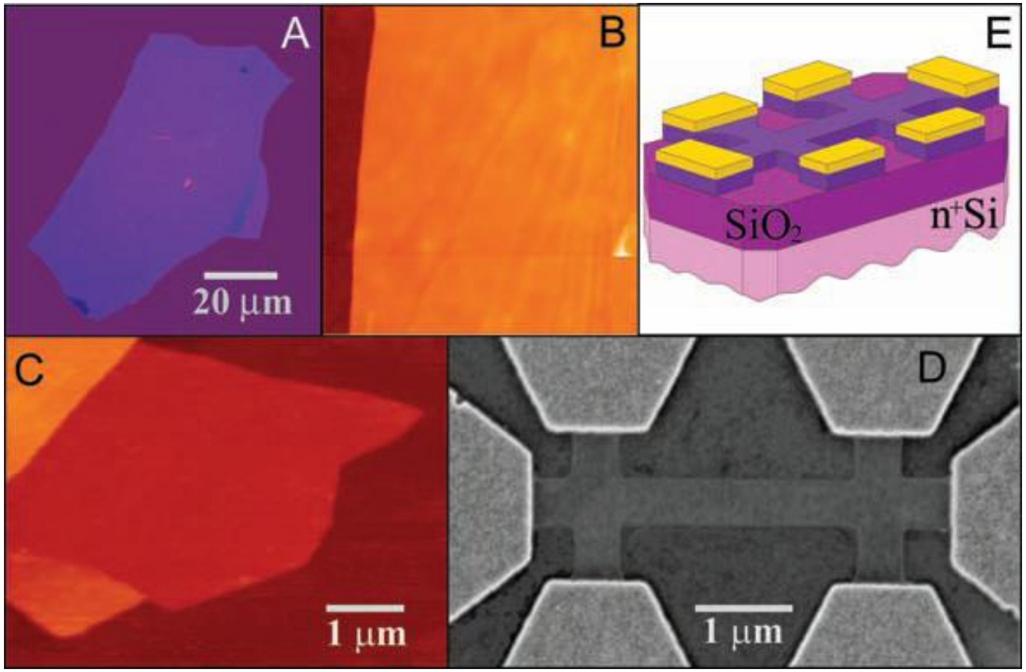


- Electric field effect in atomically thin carbon films

Novoselov, Geim, et al. Science 2004

- Two-dimensional gas of massless Dirac fermions in graphene.

Novoselov, Geim, et al. Nature 2005

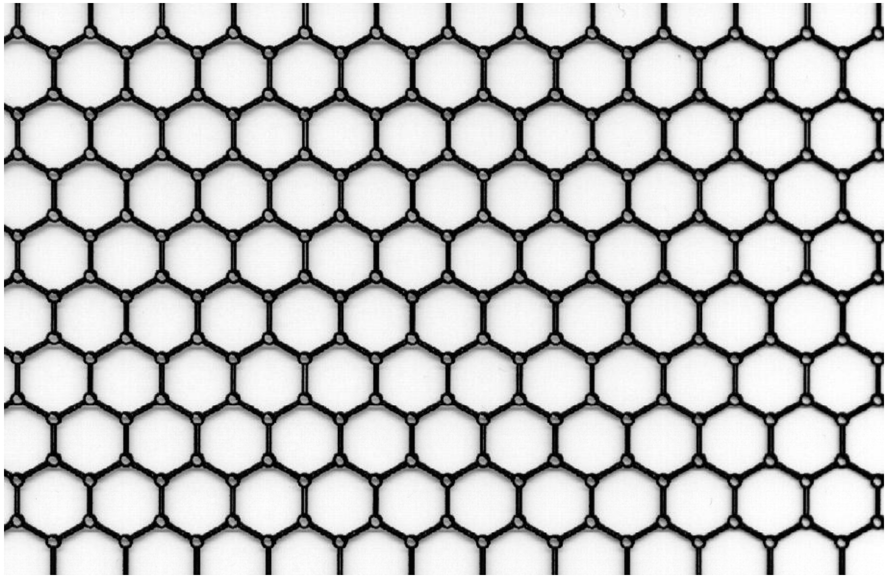


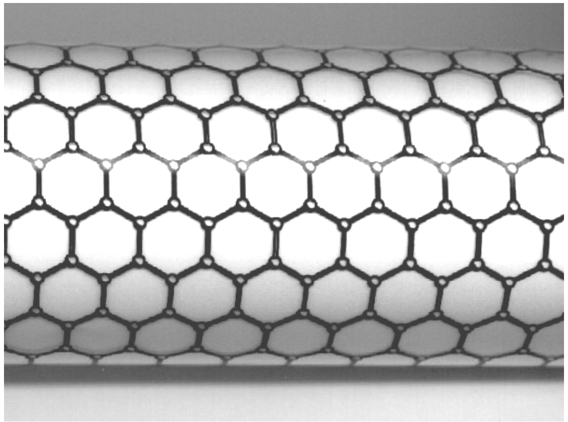
(Novoselov et al Scince 2004)

Room temperature mobility: 10,000 cm^2/Vs. Carrier concentration (electron, hole): 10^{13} cm^{-2}graphite . (GaAs-based HEMT (2D-gas): 10^{12} cm^{-2}, 6000 cm^2/Vs)

Graphene films: Repeated **peeling** of highly oriented pyrolytic graphite.

グラファイトシート　１枚からなる円筒が構造単位



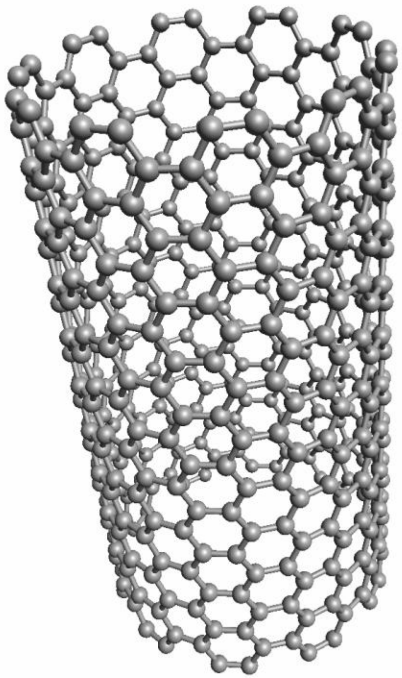


単層炭素ナノチューブ　(Single-wall carbon nanoutbe, SWNT)

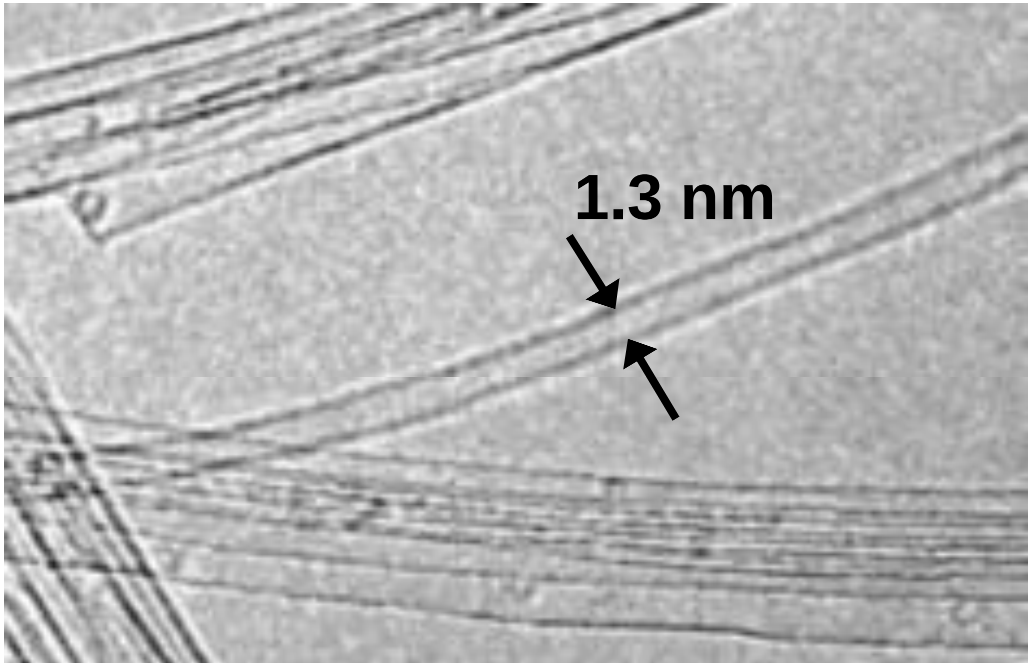
多層炭素ナノチューブ　(Multi-wall carbon nanotube, MWNT)

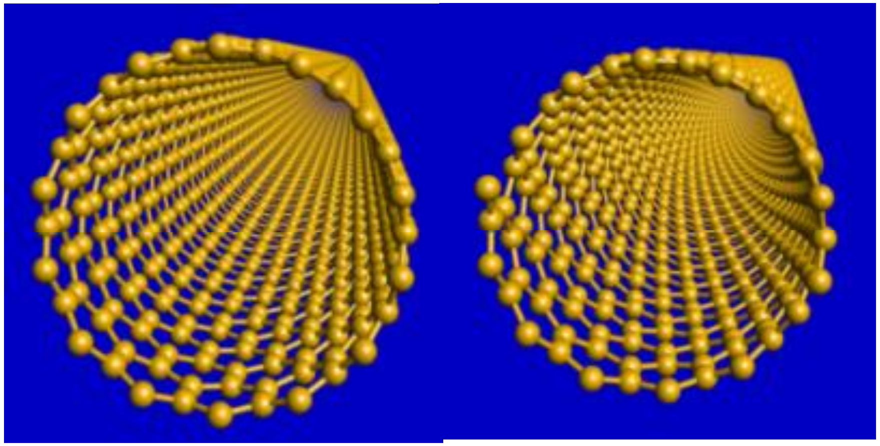
単層カーボンナノホーン　(Single-Wall carbon Nanohorn. SWNH)

1993 : Single-Wall Carbon Nanotubes Were Found.



S. Iijima, T. Ichihashi, *Nature 363*, 603, **1993**.
D. S. Bethune et al. *Nature 363*, 605, **1993**.





Φ1.3 nm: 40 C-atoms at edge

A graphene sheet forms a cylinder.
Diameter : 1.3 nm (0.4 ~ 2 nm)
Length : Micrometer order

Carbon Nanotube Research

1960 Multi-Wall Carbon Tubes with Micrometer-Order Diameters (R. Bacon)
1985 C_{60} (Kroto, Smalley et al.)
1991 Multi-Wall Carbon Nanotubes Structure: Seamless Cylinder of Graphene Sheets（Iijima）
1992 Theoretical Prediction of Electronic Structure of SWNT（Hamada et al.)
1993 Synthesis and Confirmation of SWNTs (Iijima et al.), (Bethune)
1995 Large Scale Synthesis of SWNTs (Smalley et al.)
1997 Electric Properties Measurement of Individual SWNT (Dekker et al.)
1998 FED (Y. Saito)
1998 Research on CNT Field Effect Transistors (Dekkeret al.), (Avouris et al.)
1999 SWNHs
2001 Logic Circuit (Dekker et al.)

CVD growth of SWNT
Research on the bio applications

多層カーボンナノチューブ（MWNT)

製法を大別すると‥

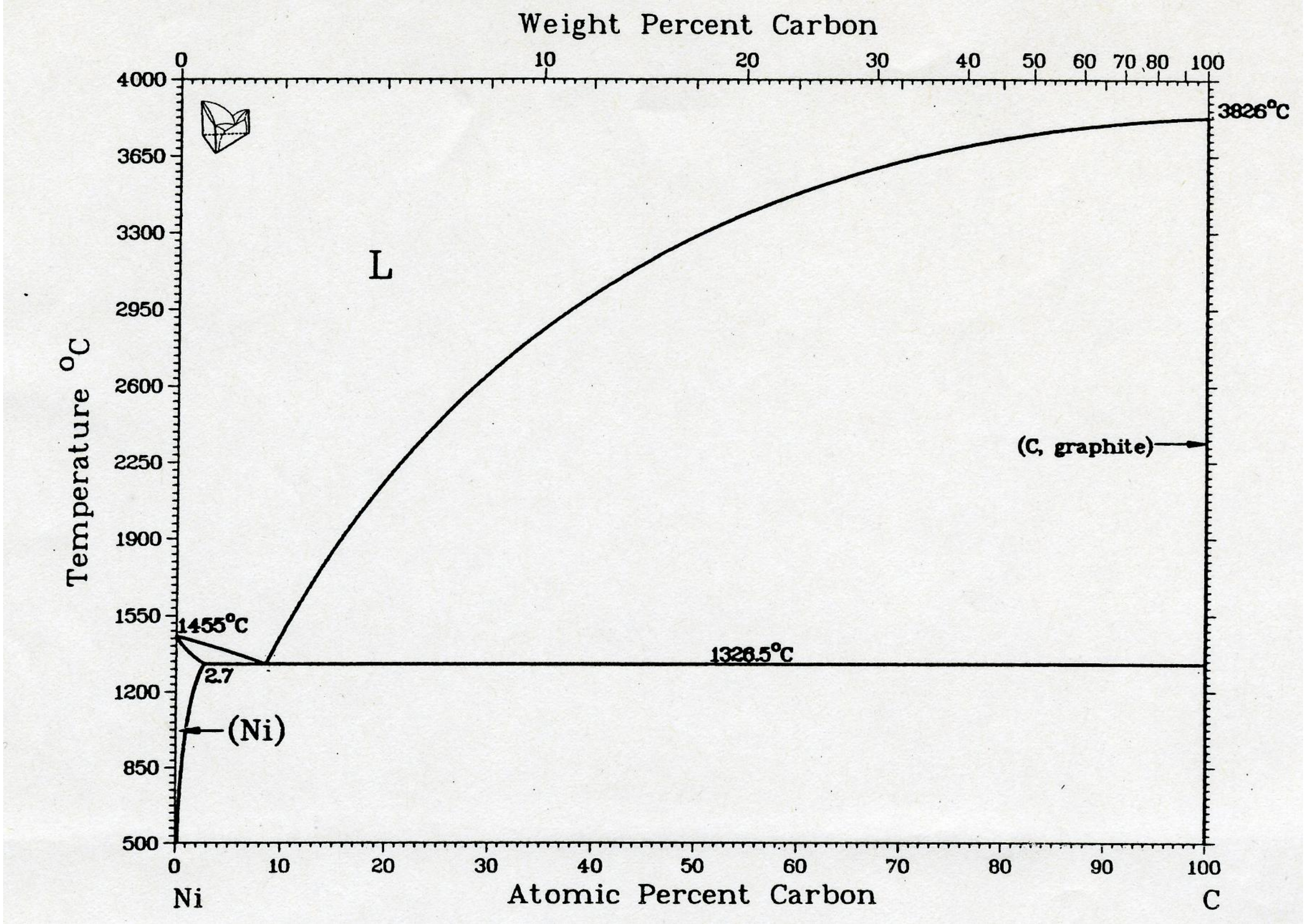
金属触媒を用いる:　気相流動法、CVD法、アーク法

金属触媒を用いない:　アーク法、HFプラズマ法

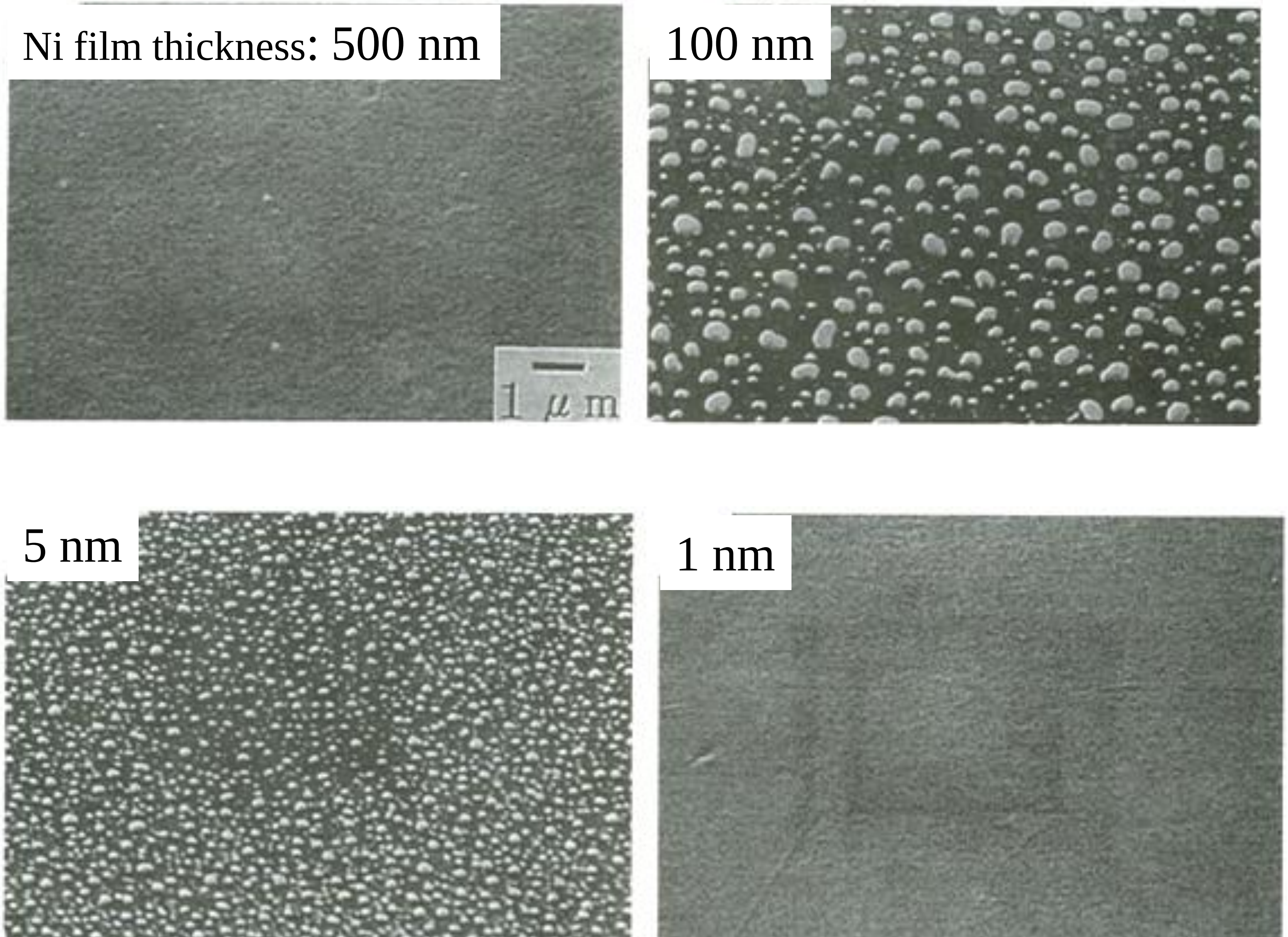
多層カーボンナノチューブのターゲット用途　(樹脂複合材料分野)

三井物産

Metal-Carbon Phase Diagram

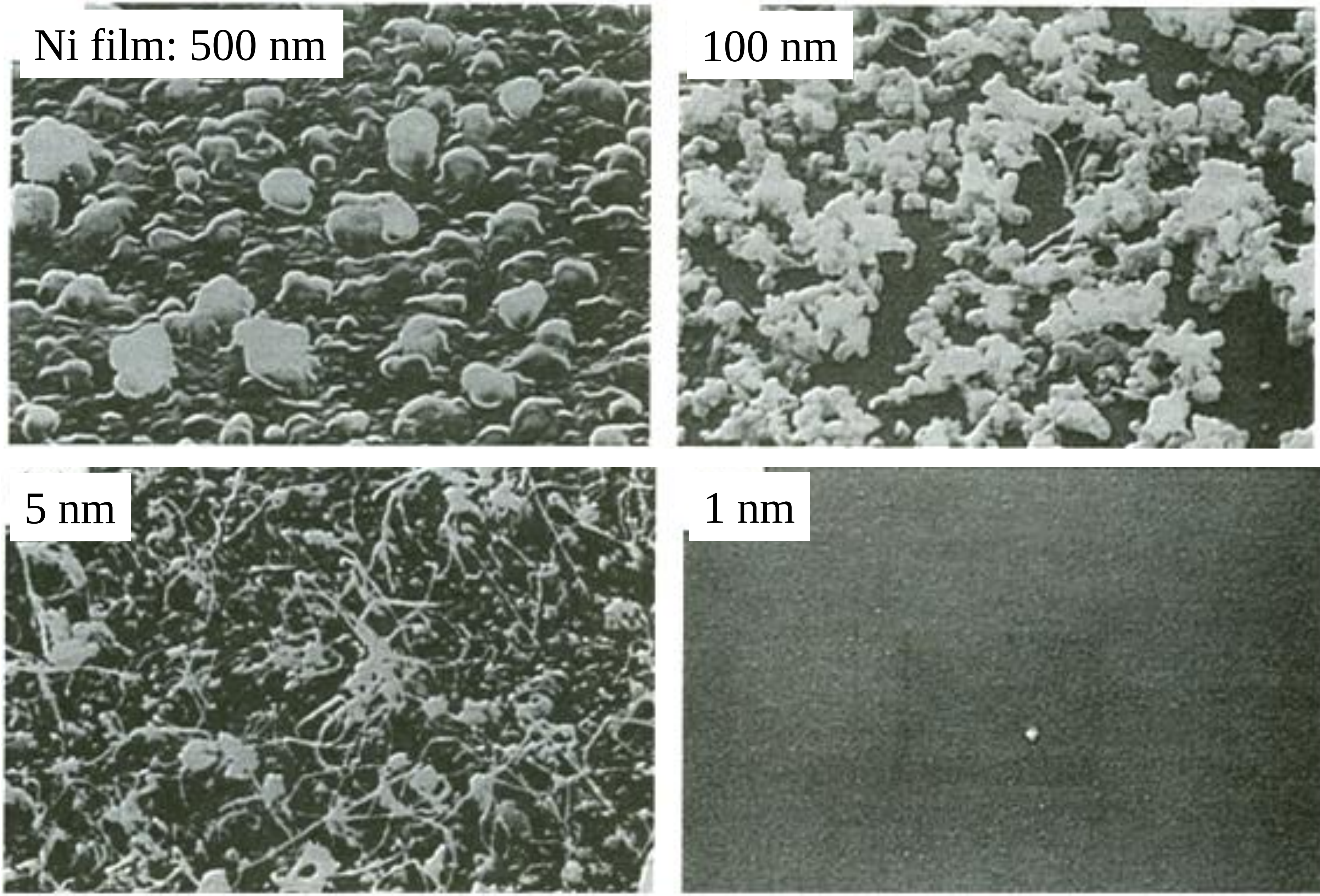


After heat treatment at 700°C

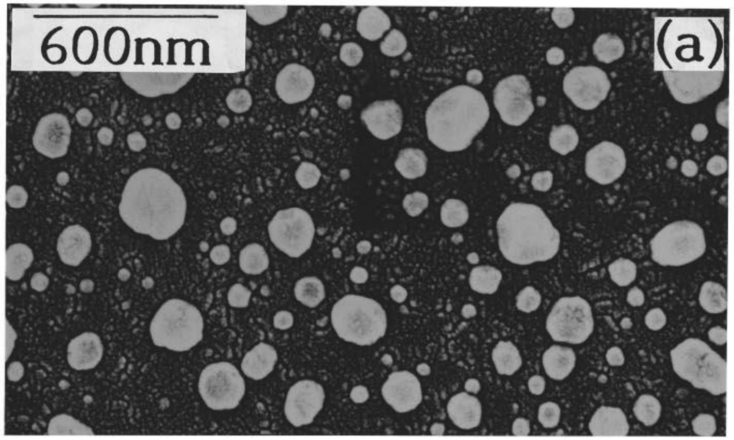


Yudasaka et al. Thin Solid Films

After CVD at 700^{o}C

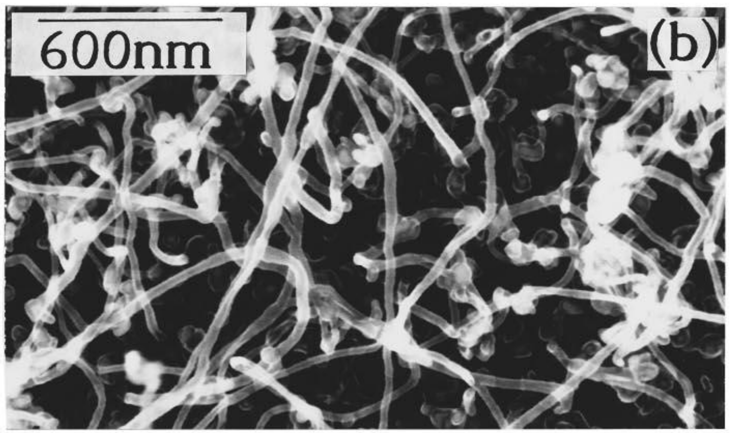


Yudasaka et al. Thin Solid Films

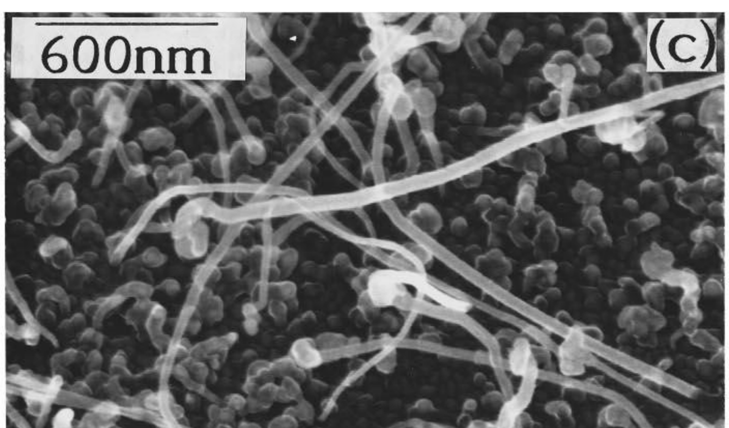


Thermal annealing

Ni films/glass → Ni particles



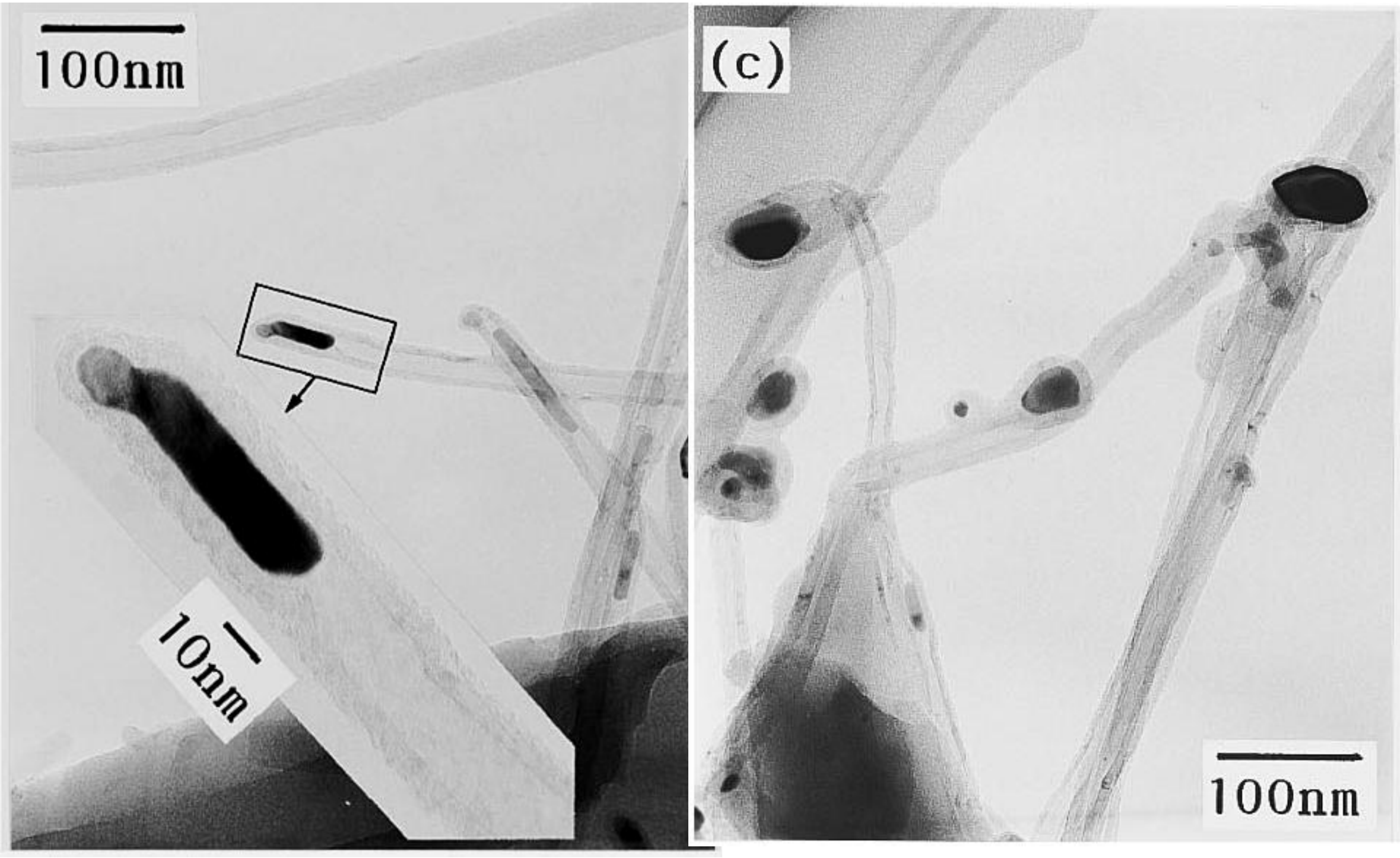
Chemical vapor deposition at 700^{o}C for 5 hours. Carbon source: Organic molecules (2-methyl-1, 2'-naphthyl ketone)



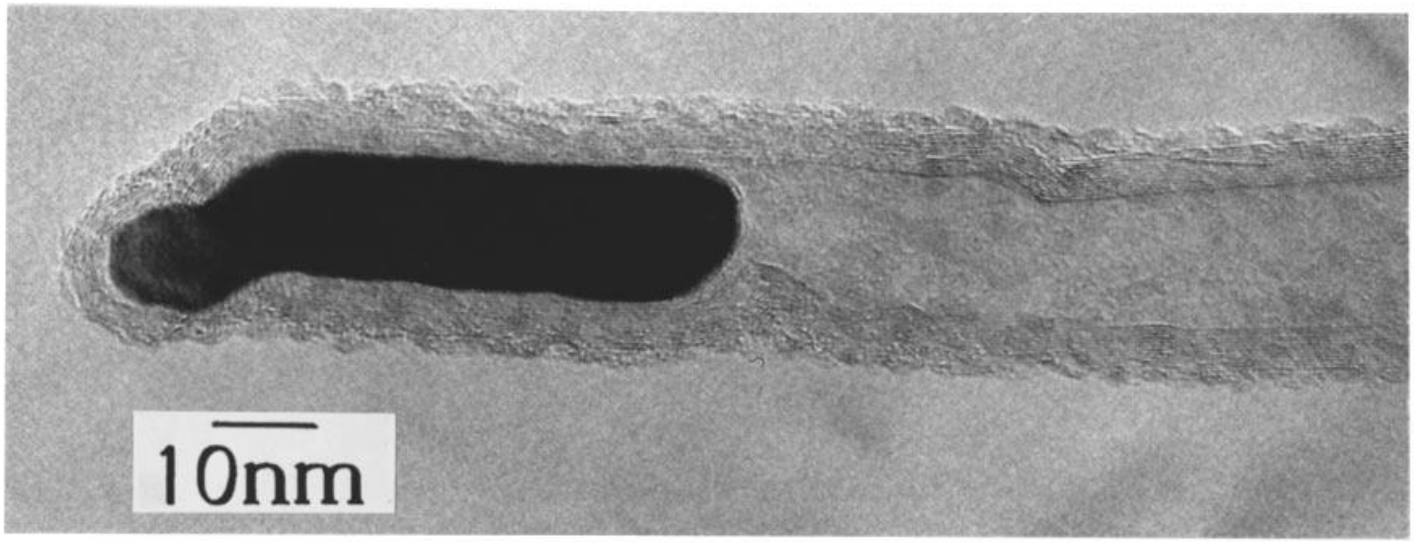
Chemical vapor deposition at 600^{o}C for 5 hours

Yudasaka et al, APL 1997

MWNT growth nucleation depending on Ni particle zies

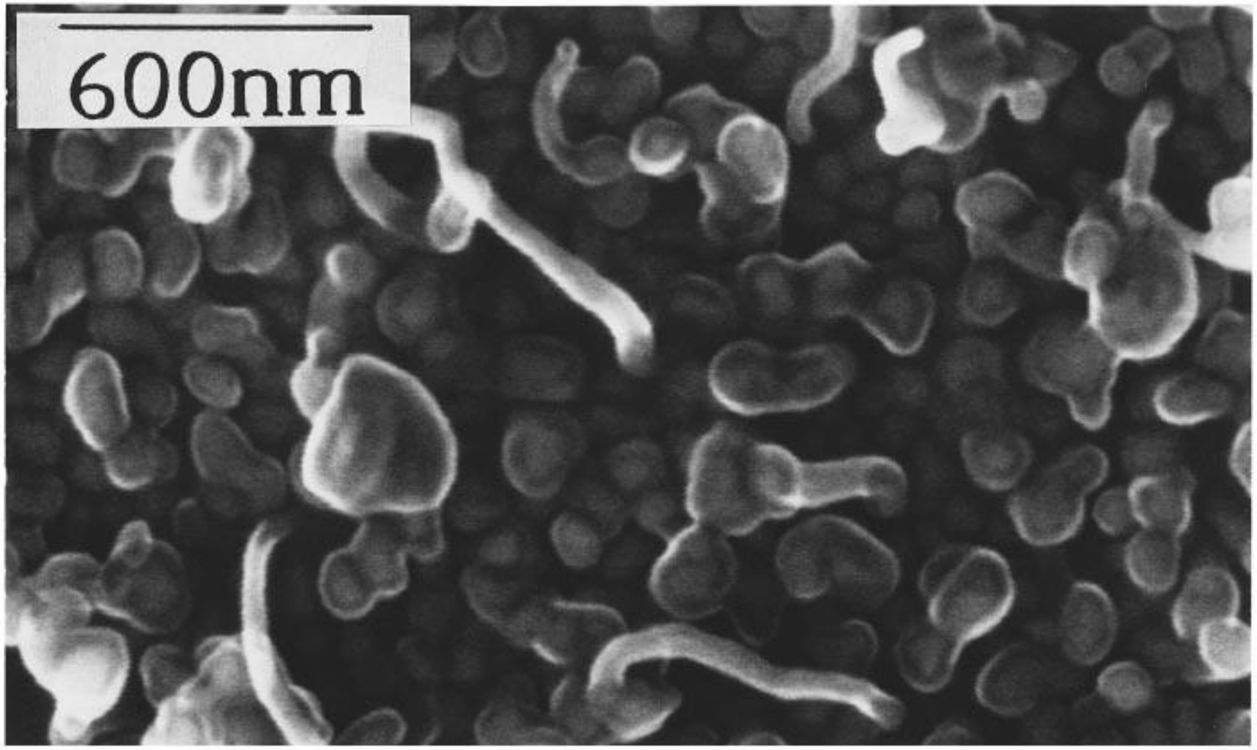


How to explain?



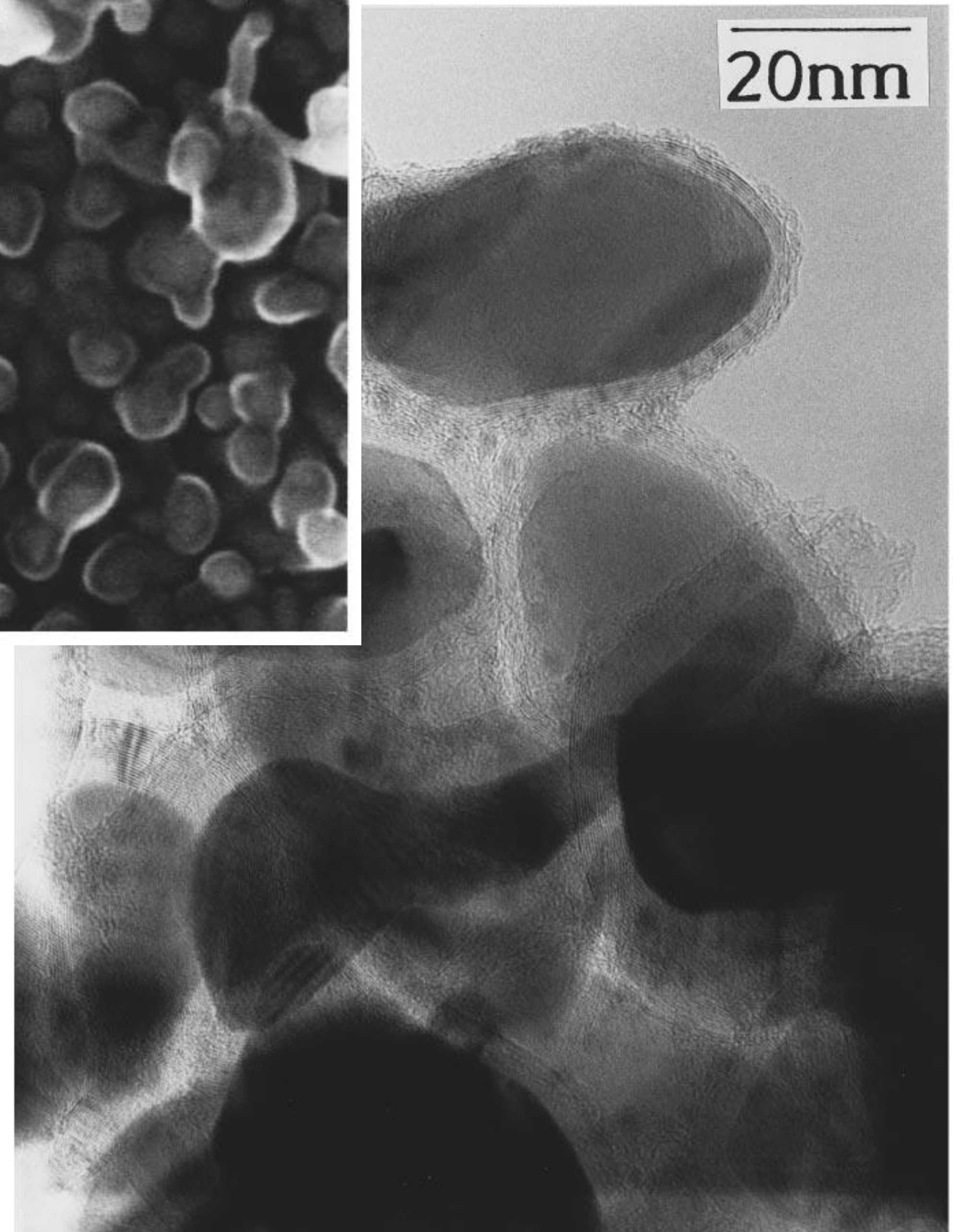
CVD at 700^{o}C for 5 hours

Yudasaka et al, APL 1997



SEM

TEM

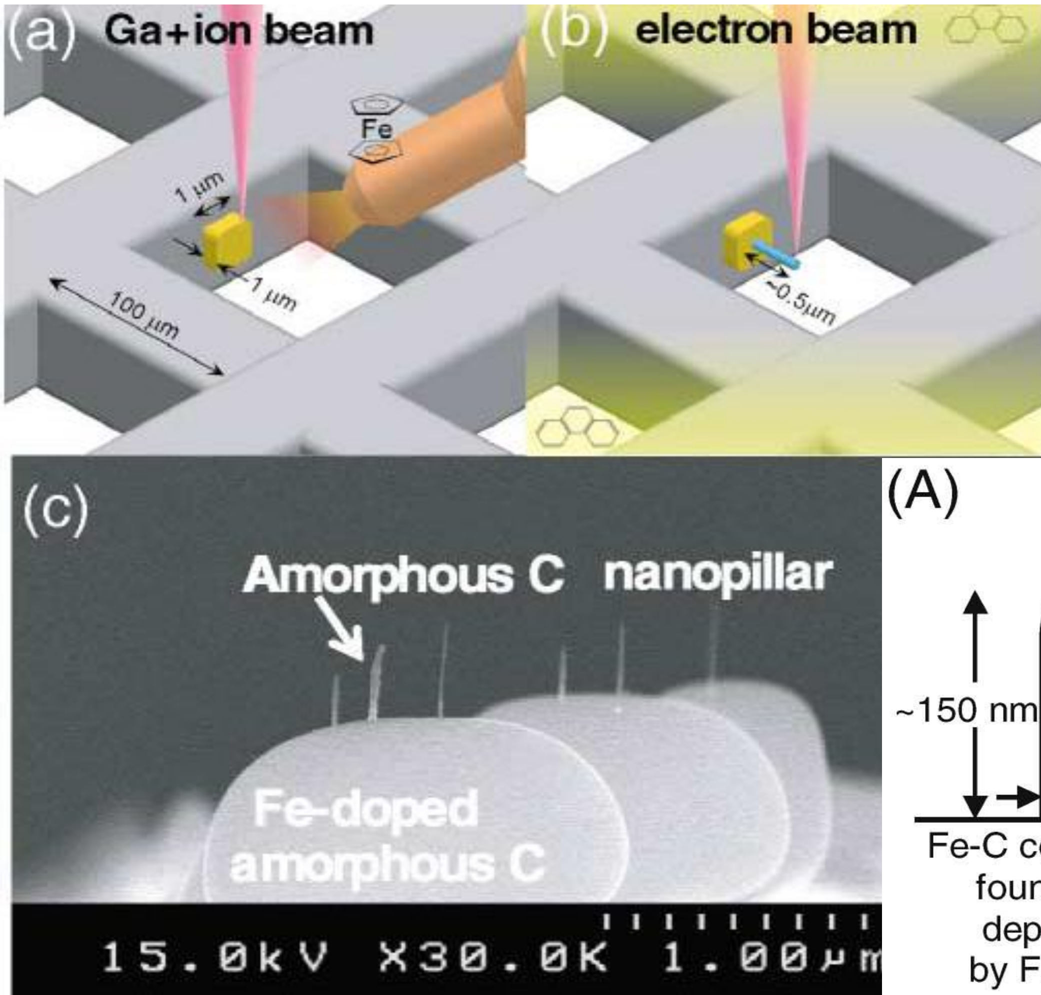


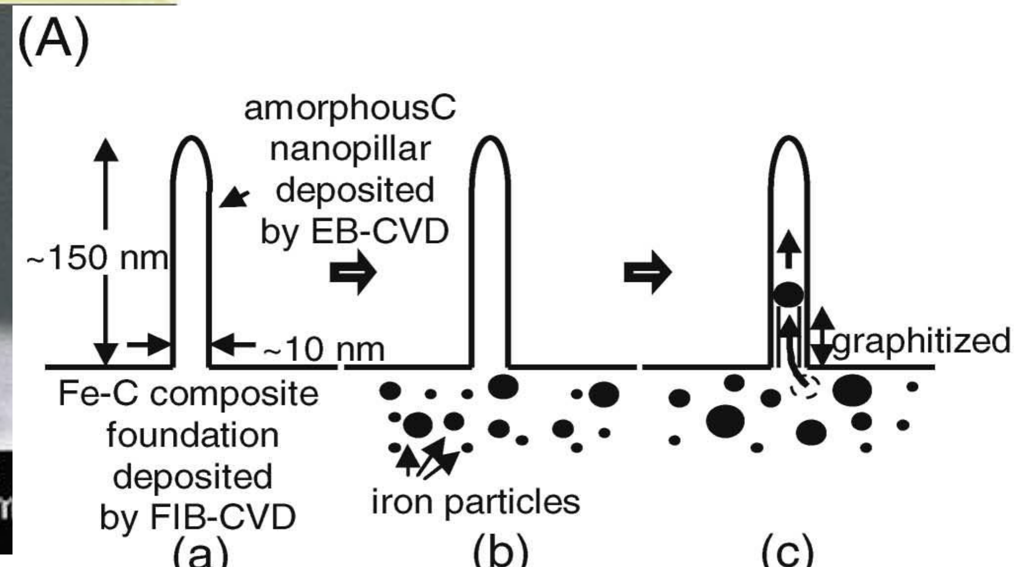
CVD for **30 minutes**

Yudasaka et al, APL 1997

In situ Observation of Carbon-Nanopillar Tubulization Caused by Liquidlike Iron Particles

Ichihashi, Fujita, Ishida, and OchiaiPRL *92*(**2004**)

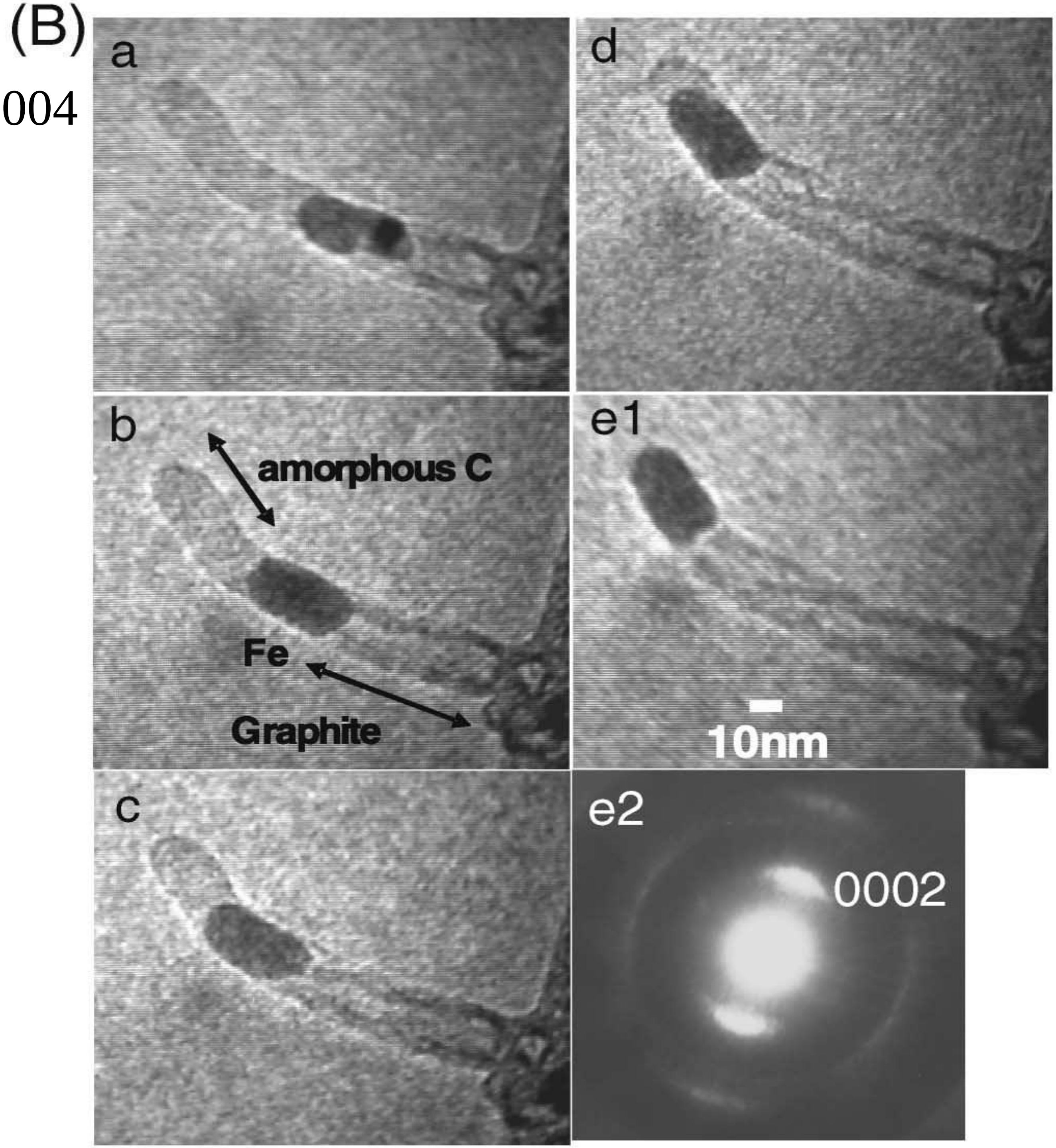


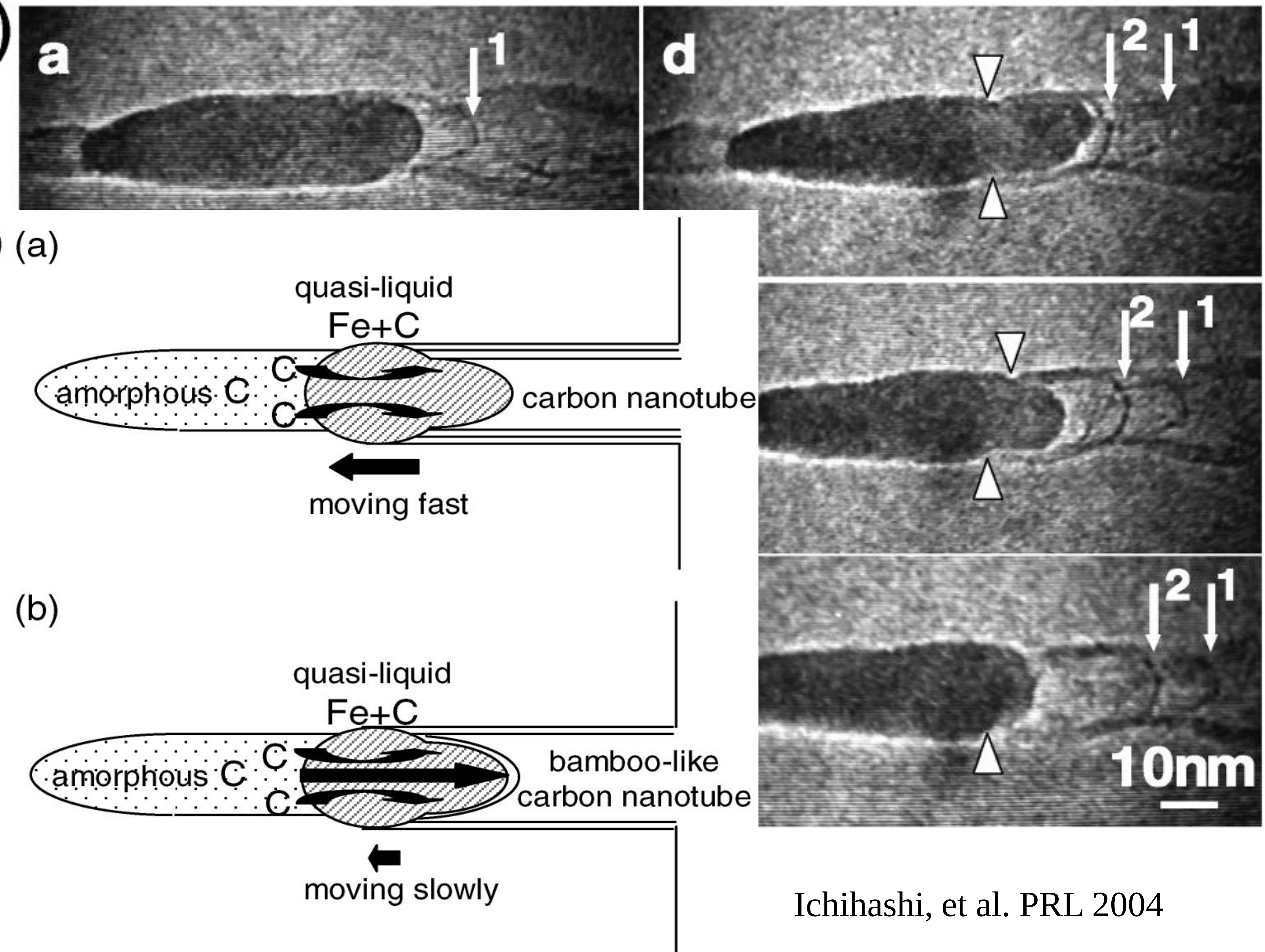


Ichihashi, et al. PRL 2004

加熱 650^{o}C

2秒ごとに撮影

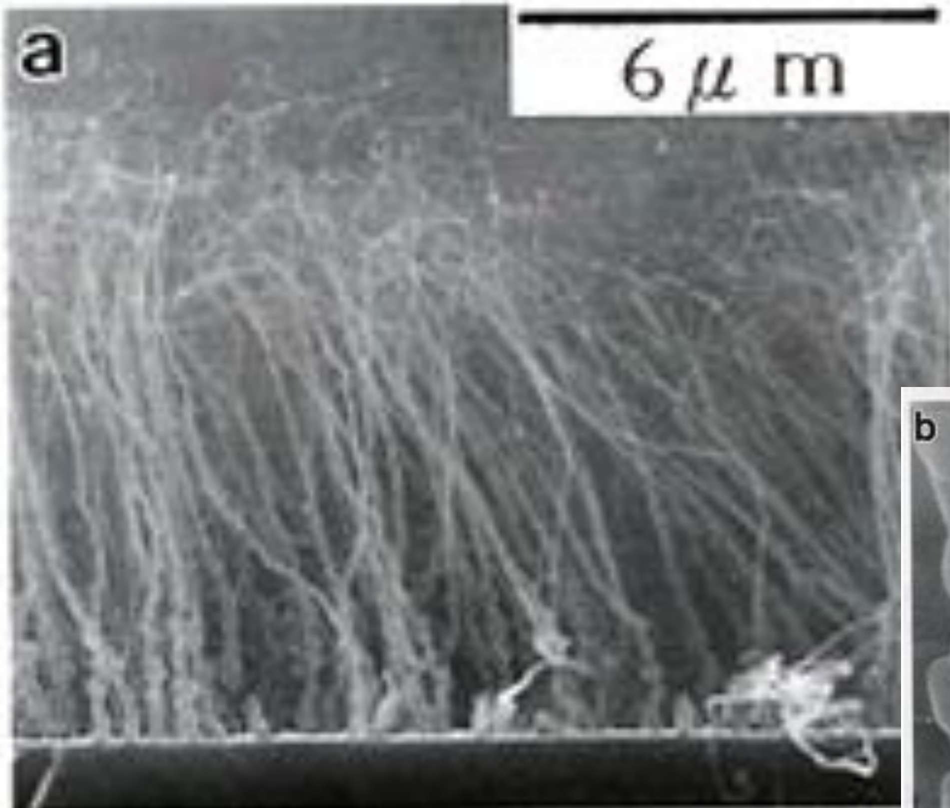




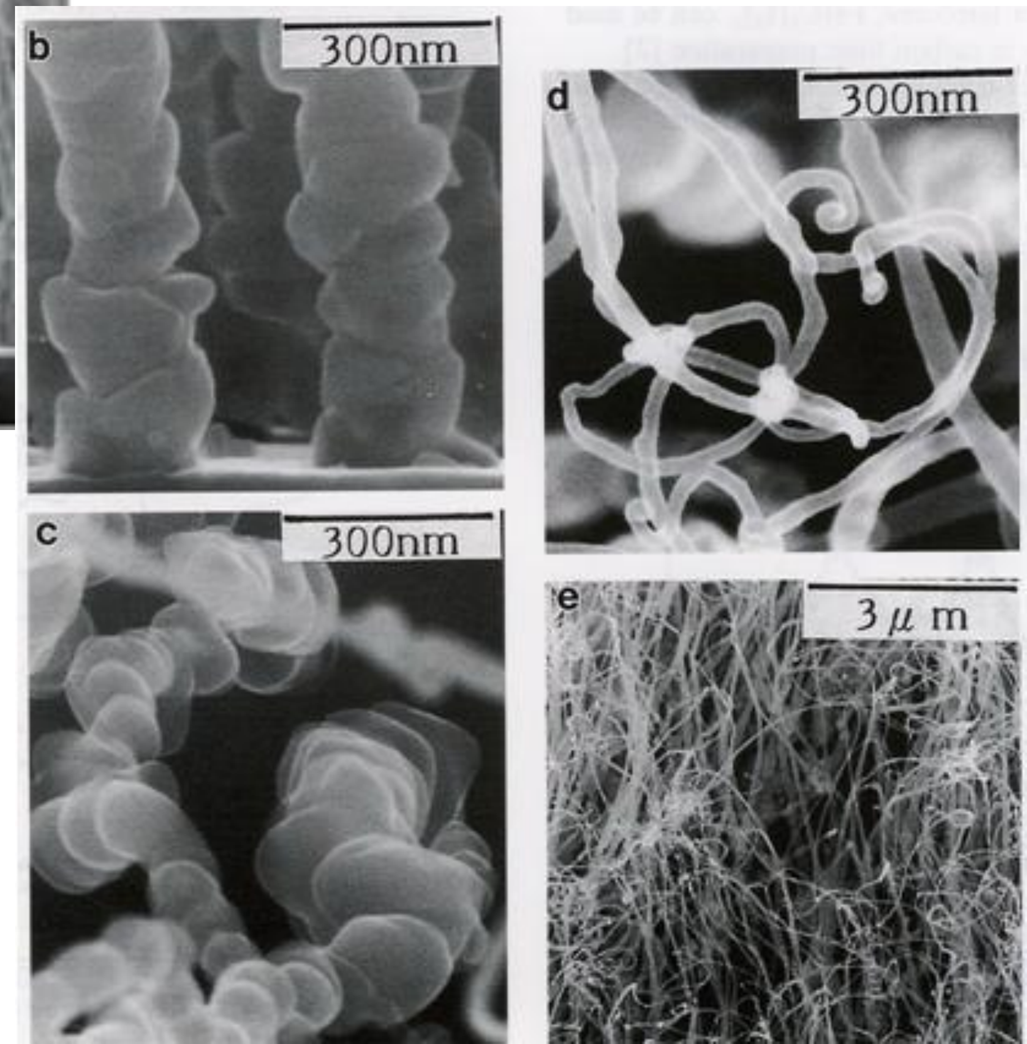
Ichihashi, et al. PRL 2004

Growth model of MWNT

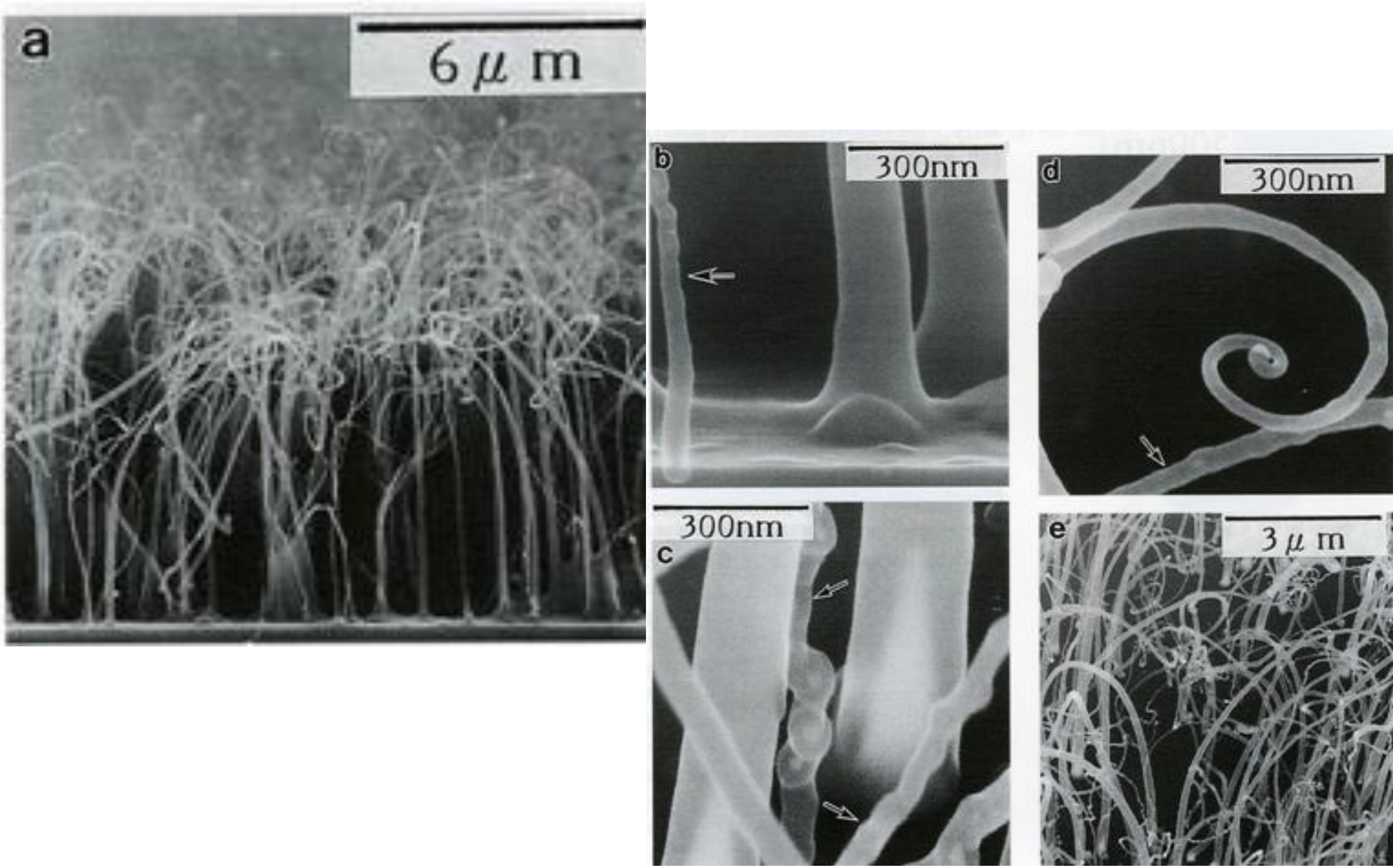
- Large Ni particle (50 nm <)
- Medium (20-30 nm)
- Small (<10 nm)



CVD 800^{o}C
Starting material: NiPc

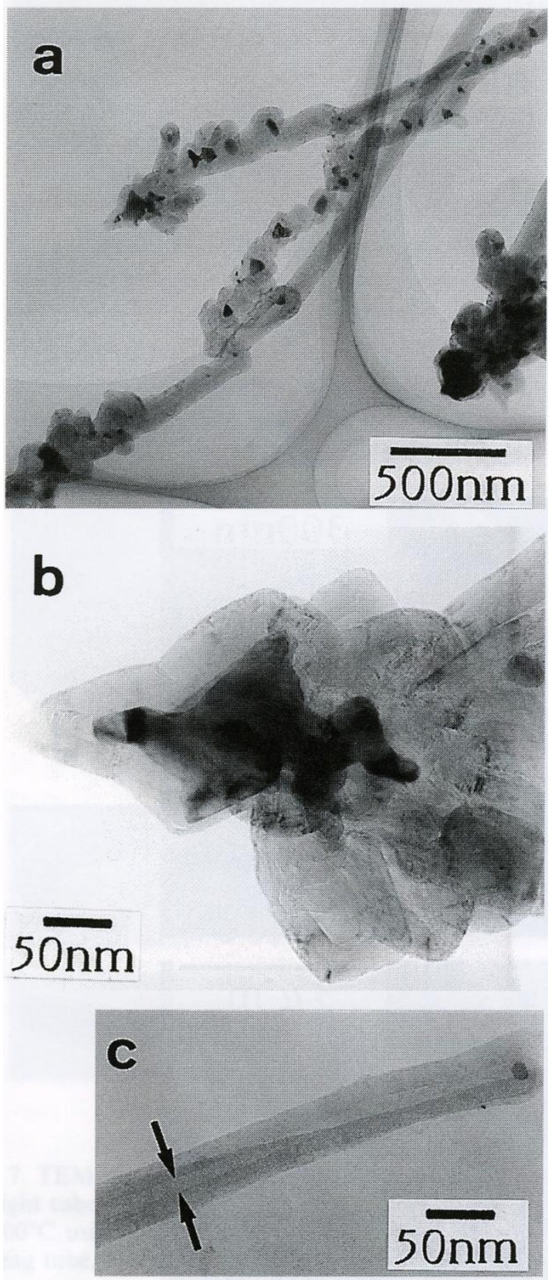


Yudasaka et al 1997 Carbon

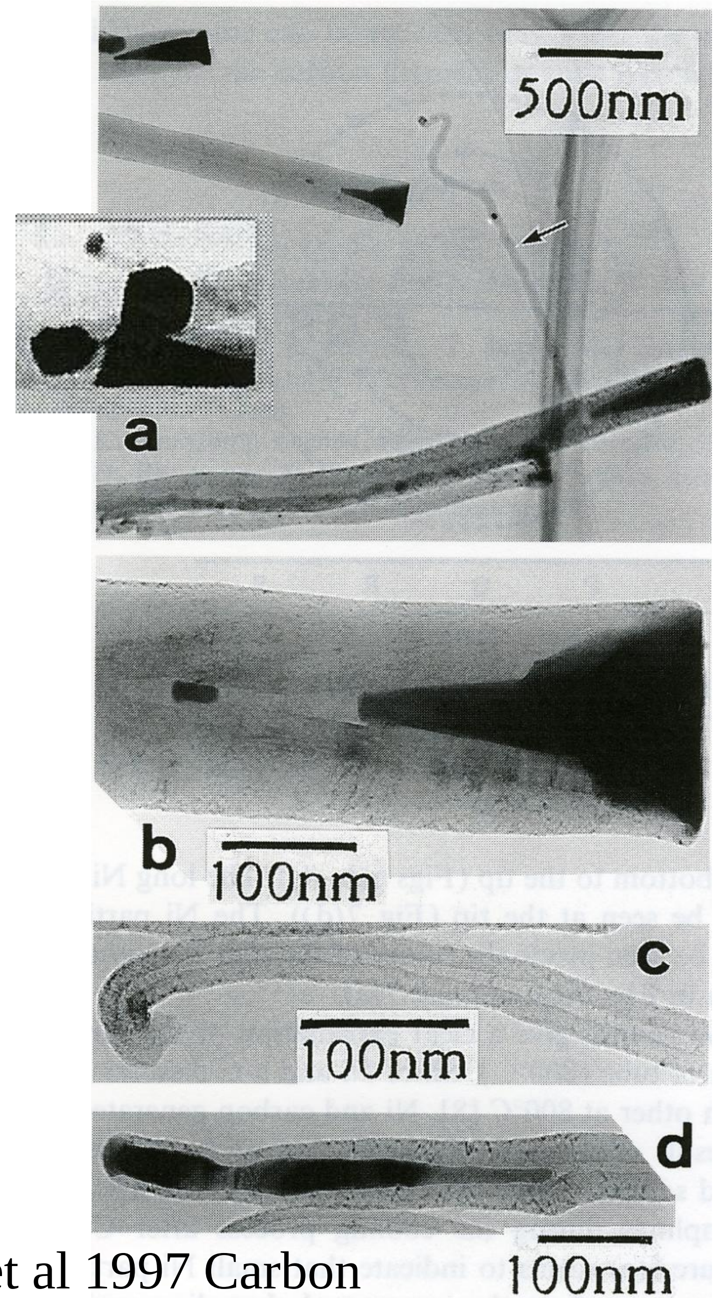


Yudasaka et al 1997 Carbon

NiPc-CVD 800°C

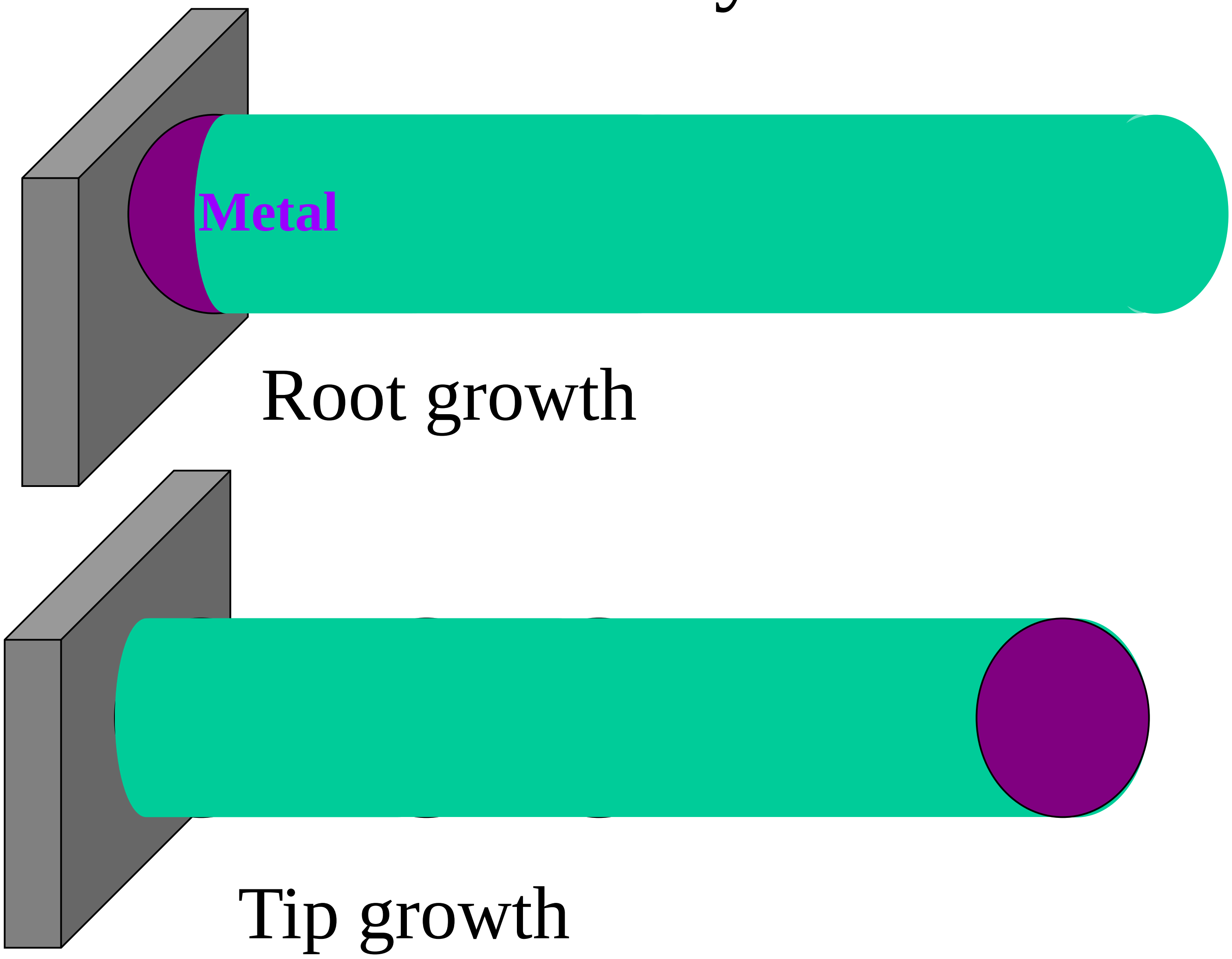


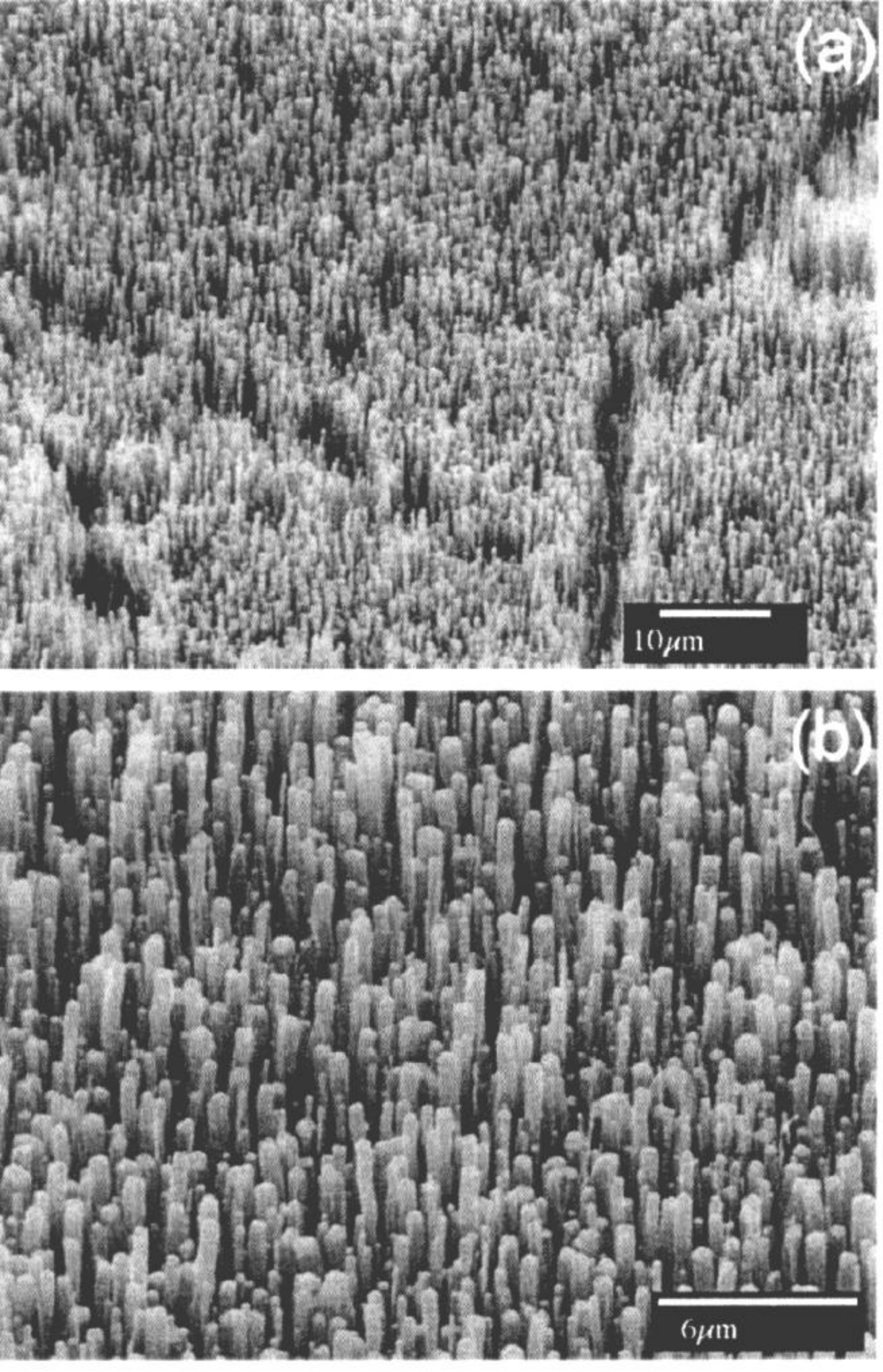
NiPc-CVD 700°C



Yudasaka et al 1997 Carbon

MWNT growth mechanism.
Metal catalyzed.

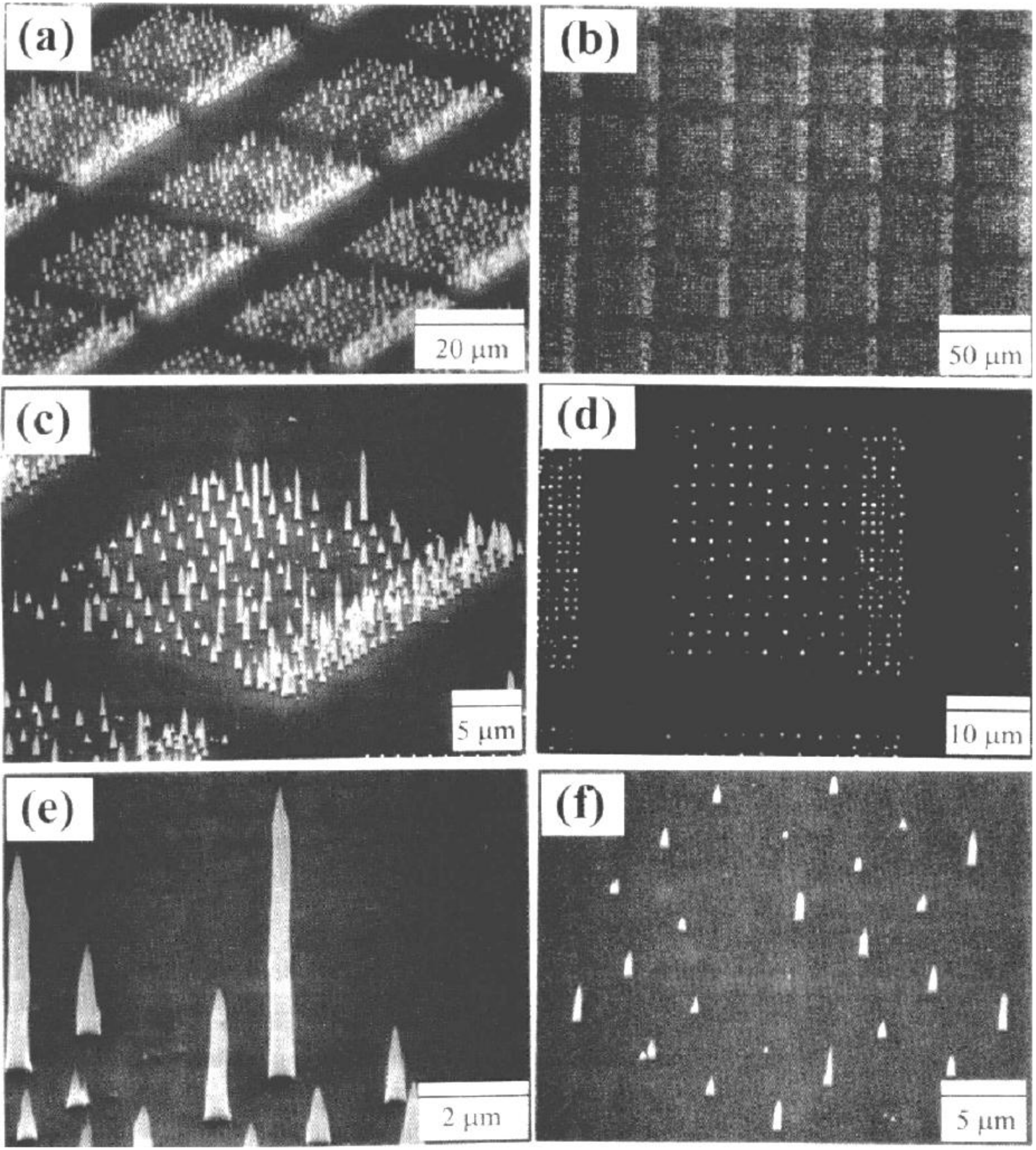




Plasma-enhanced hot filament CVD

1-20 Torr acetylene, ammonia
Ni (on display glass of Corning Inc.)
Tungsten filament coil
Plasma generator
Estimated sample temperture <666^{o}C
10min – 5h

Z. P. Huang et al. Appl. Phys Lett. 73(1998)3845.



Site selective growth of MWNTs

Z. F. Ren
Appl. Phys. Lett. 75, 1086(1999)

011210b

Metal-free synthesis of MWNT

Grumbach and Martin, PRB 54(1996)15730

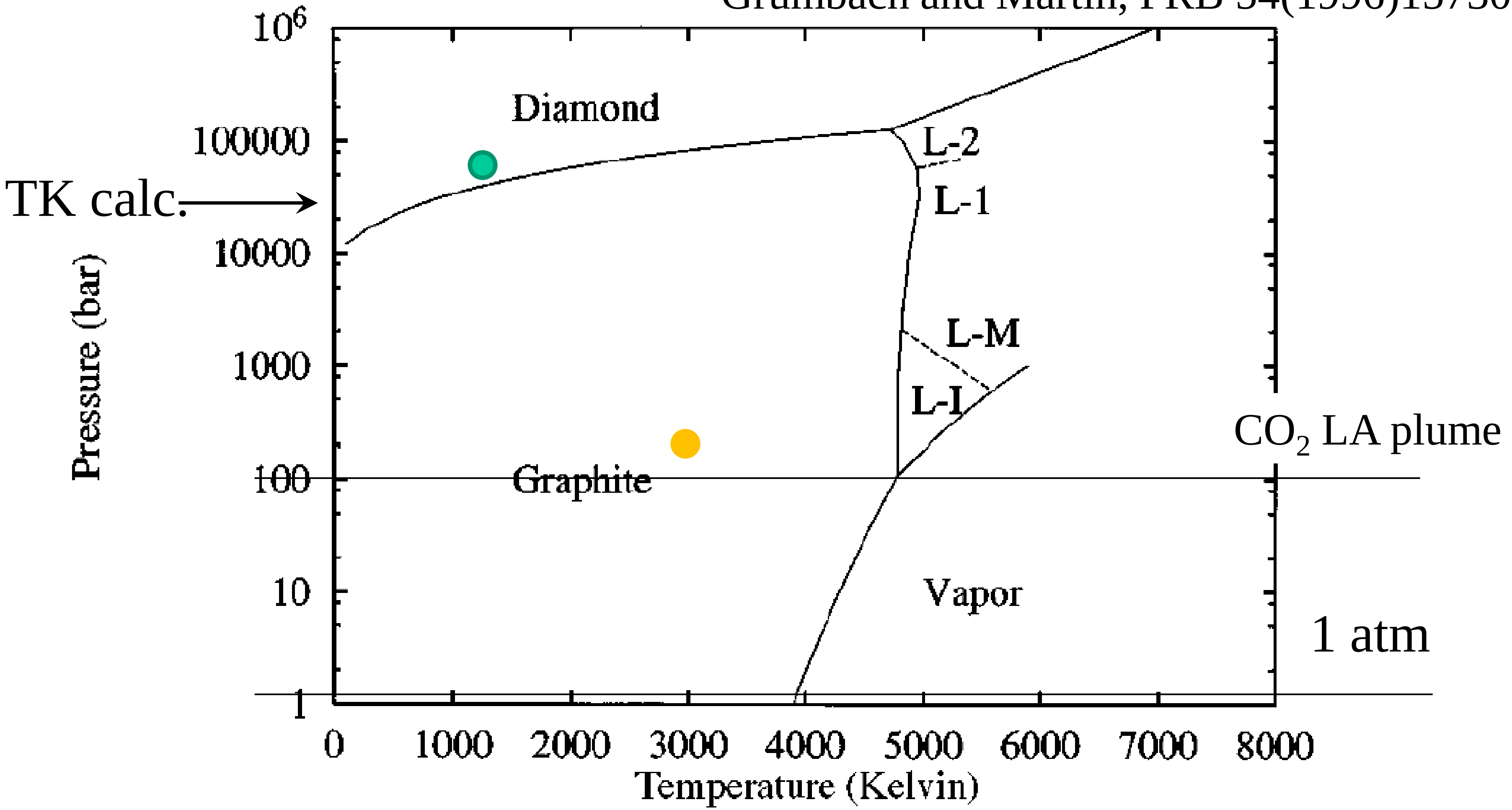
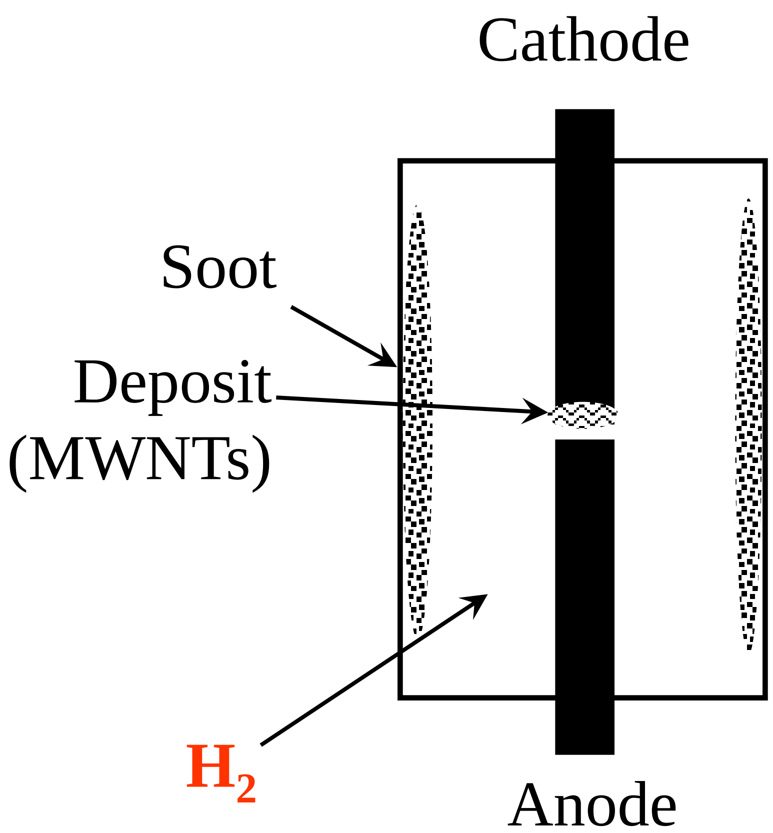


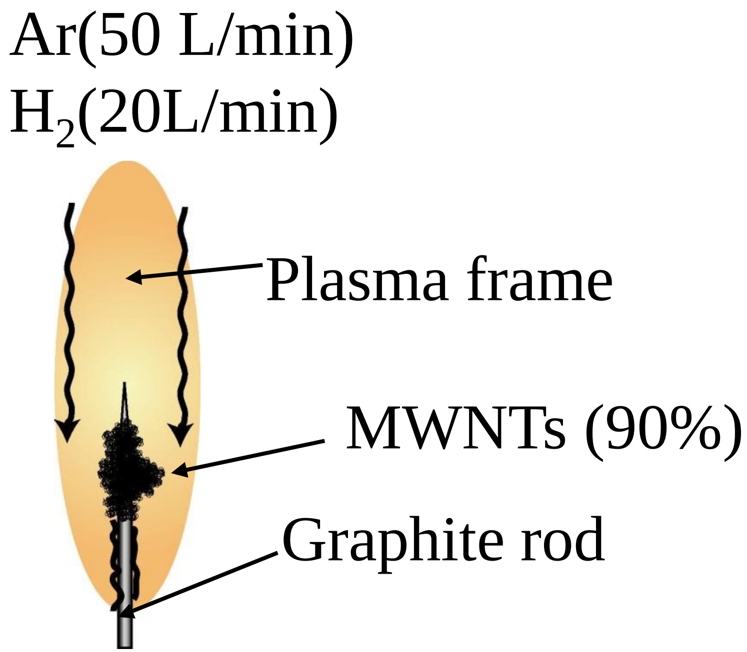
FIG. 1. Phase diagram of carbon at low pressures. Solid lines indicate phase boundaries for which some experimental evidence exists (Ref. 14). Dashed lines indicate theoretically proposed phase boundaries: liquid insulator (*L-I*) to liquid metal (*L-M*) (Ref. 15) and graphitelike liquid (*L*-1) to diamondlike liquid (*L*-2) (Ref. 16).

Arc discharge with graphite rods in H_2 atmosphere.



Anode evaporation rate:	**10 mg/s**
Yield (a-C soot or cathode deposits):	**50%**
Purity of MWNTs at cathode:	**Low**

Evaporation of graphite with HF plasma torch in Ar/H_2 atmosphere



- No electric fields
- Ions

Koshio, Yudasaka, Iijima, *Chem. Phys. Lett.* **356**(2002)595.

Evaporation rates of graphite, yields, and purity. HF plasma method produces high-quality MWNTs.

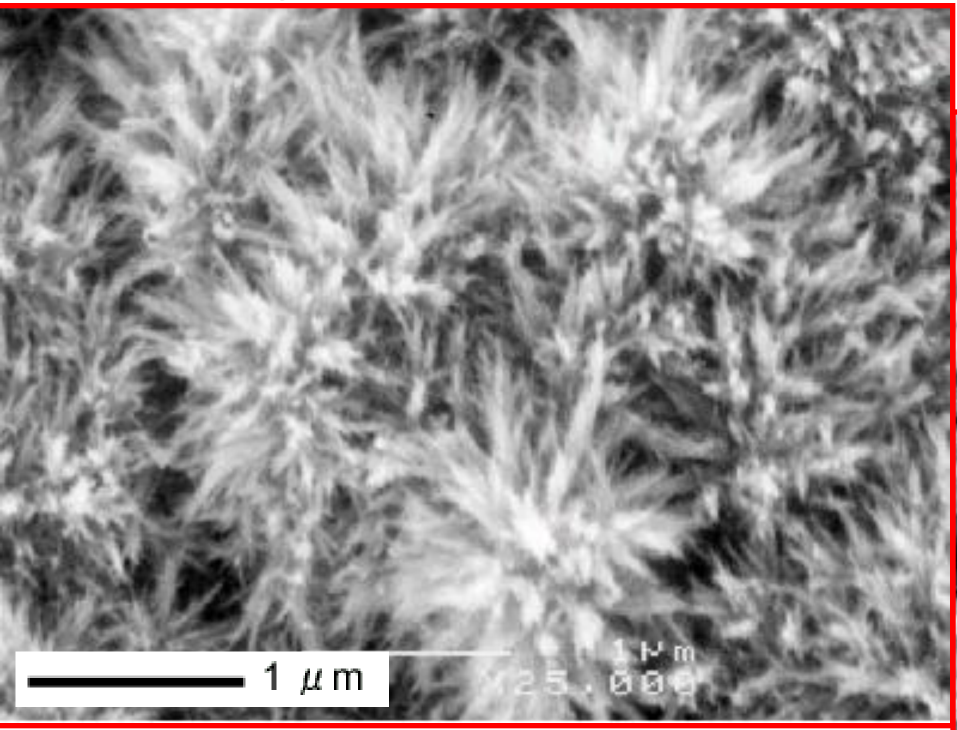
Methods	Anode evaporation	Yields	Purity
Arc discharge	10 mg/s	< 30% (cathode deposit)	Low
HF plasma	**0.005 mg/s**	**~100%**	**95%**

Ultimate MWNTs

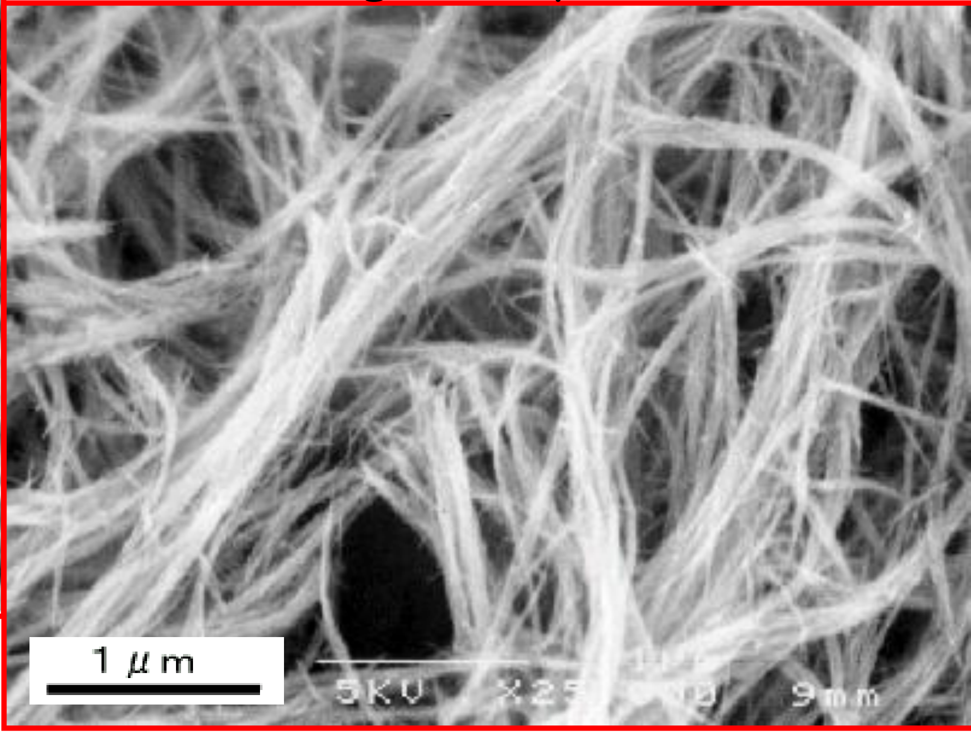
A. Koshio, M. Yudasaka, S. Iijima
Chem. Phys. Lett. **356**(2002)595.

- Fully-Packed
- Highly graphitized
- Outside-diameter selective
- 95%-Purity
- Large scale production

φ(in): 0.4 nm, φ(out): 4 nm
length : micrometer order

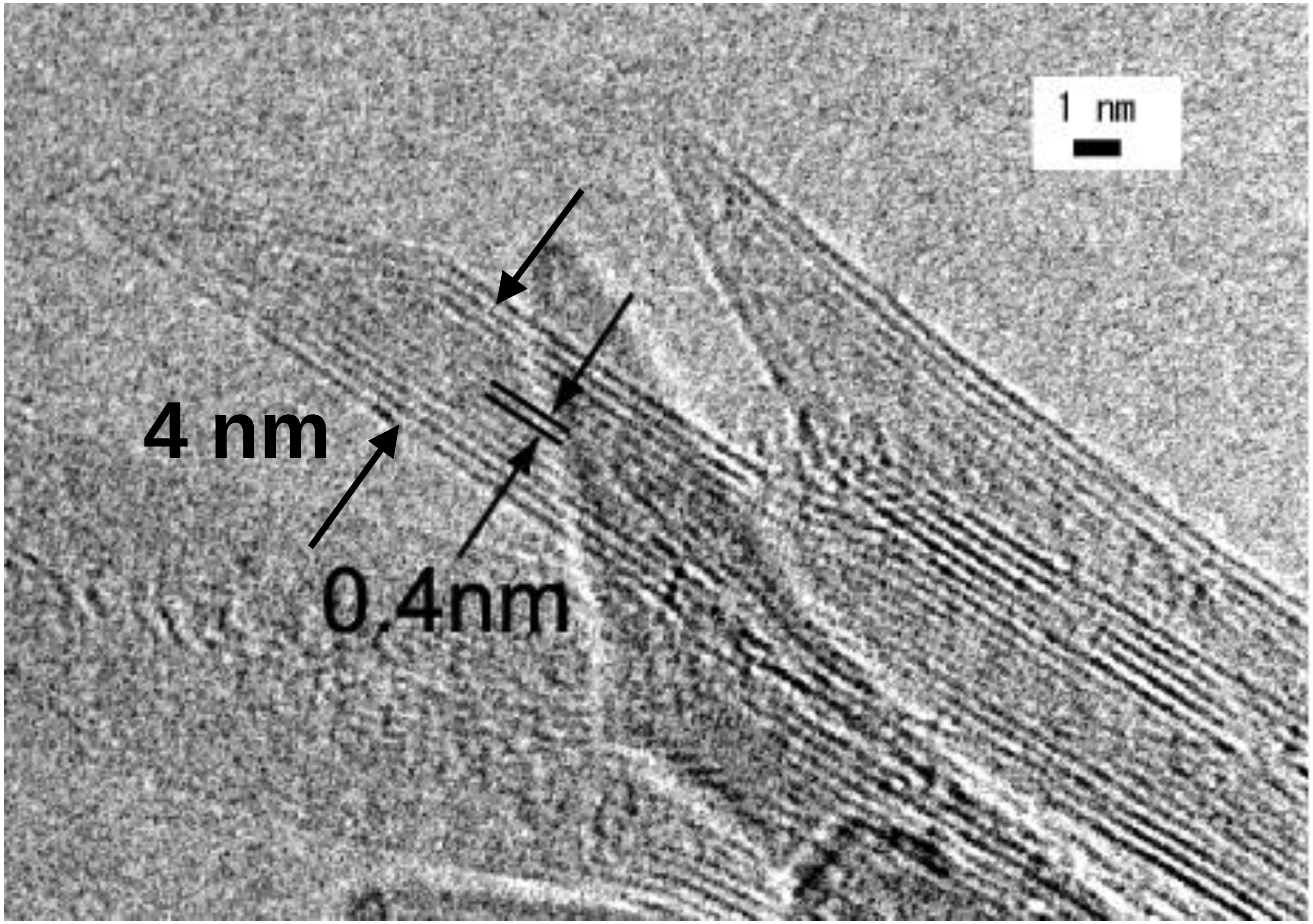


φ(in): 0.4 nm, φ(out): 20 nm
length :~10 µm

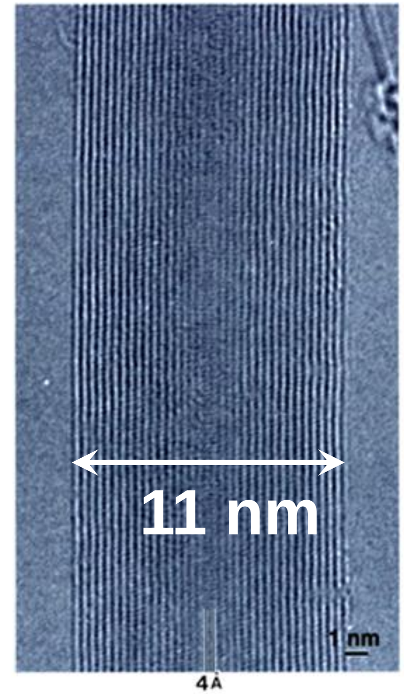


020226a

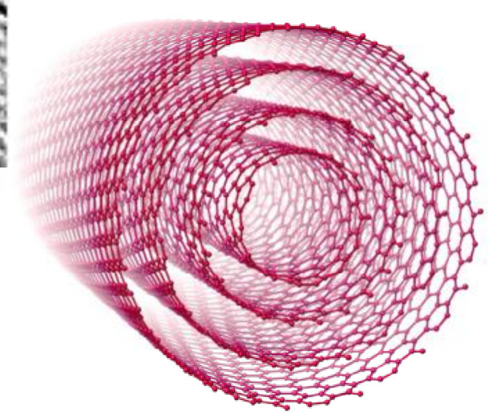
Concentric MWNTs with small outside-diameters



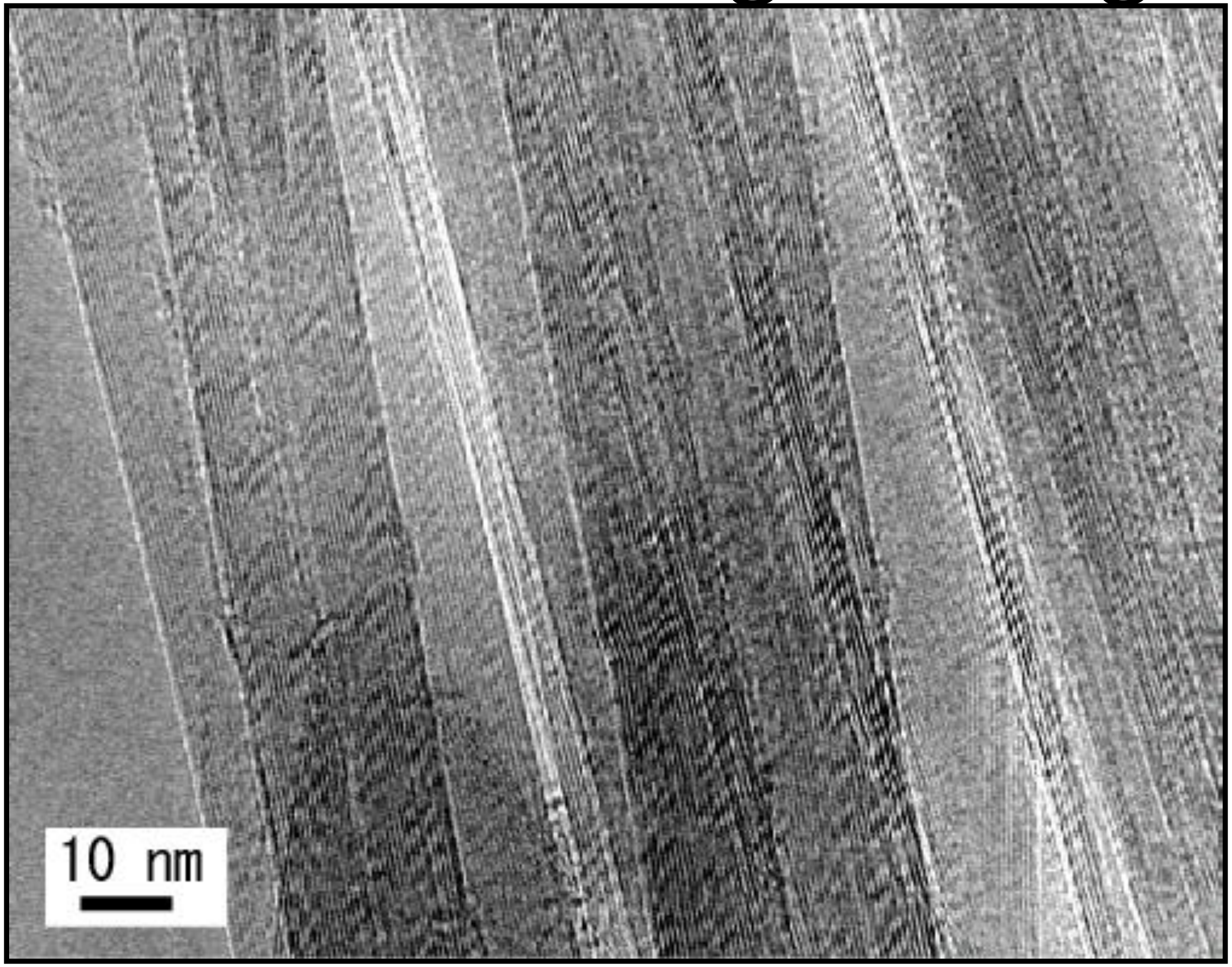
A. Koshio, M. Yudasaka, S. Iijima
Chem. Phys. Lett. **356**(2002)595.



Qin et al. *Nature* **408**(2000)408.



A TEM image of long bundles



Diameters: ~20 nm
(~30 layers)

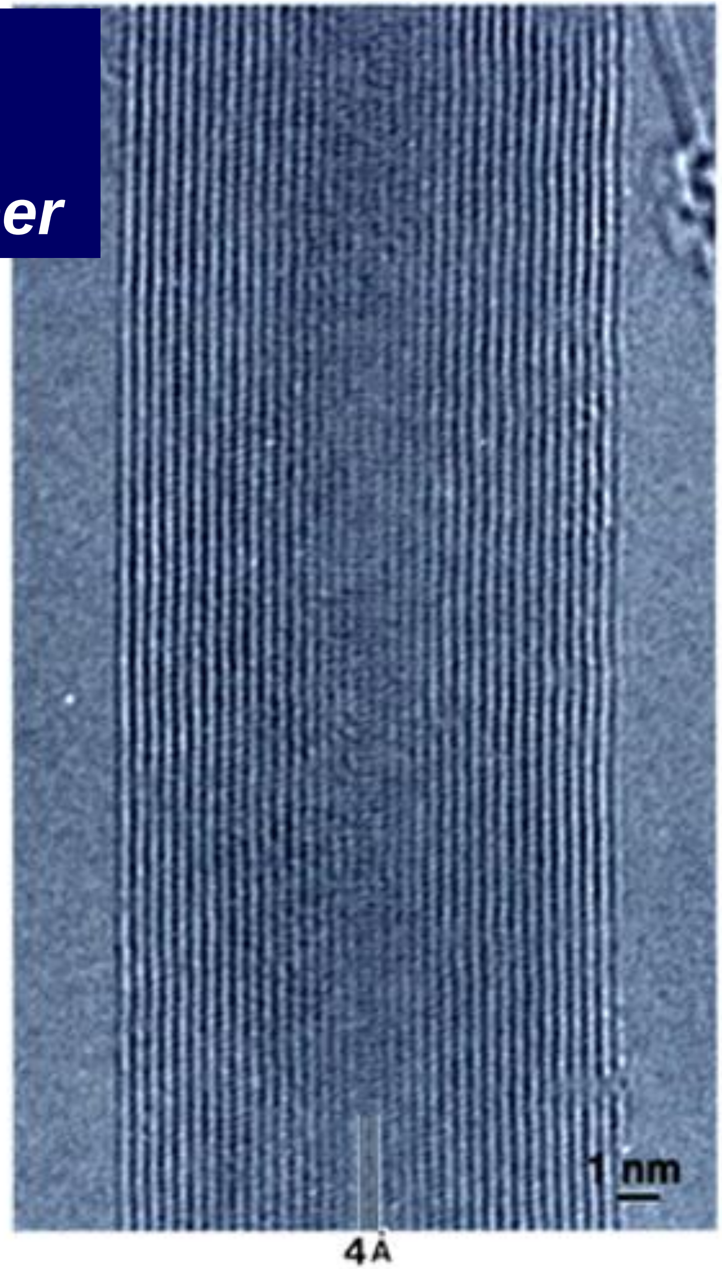
最高密度のMWNT: Densist MWNT or Densist Nanografiber

A little formed by arc-discharge in H_2.

↓

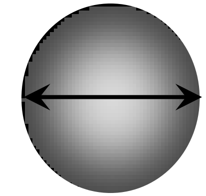
Purity of about 95% available by HF plasma.

Koshio, Yudasaka, Iijima
Fullerene Symposium 2001

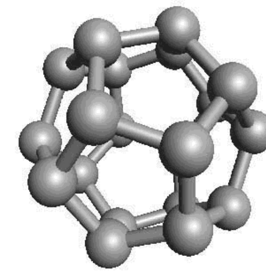


Qin, et al.

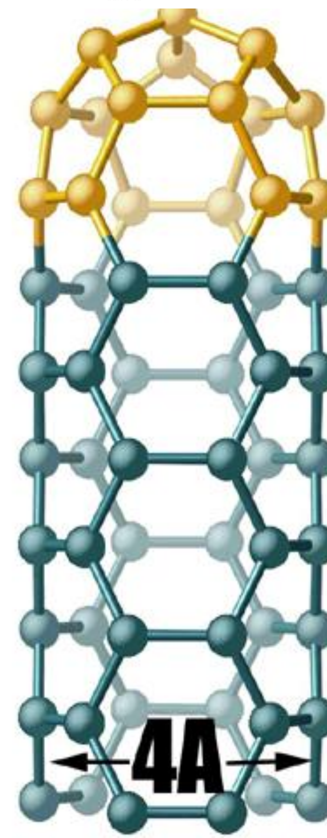
Nature 408, 50 (2000).



Au
~ 0.3 nm



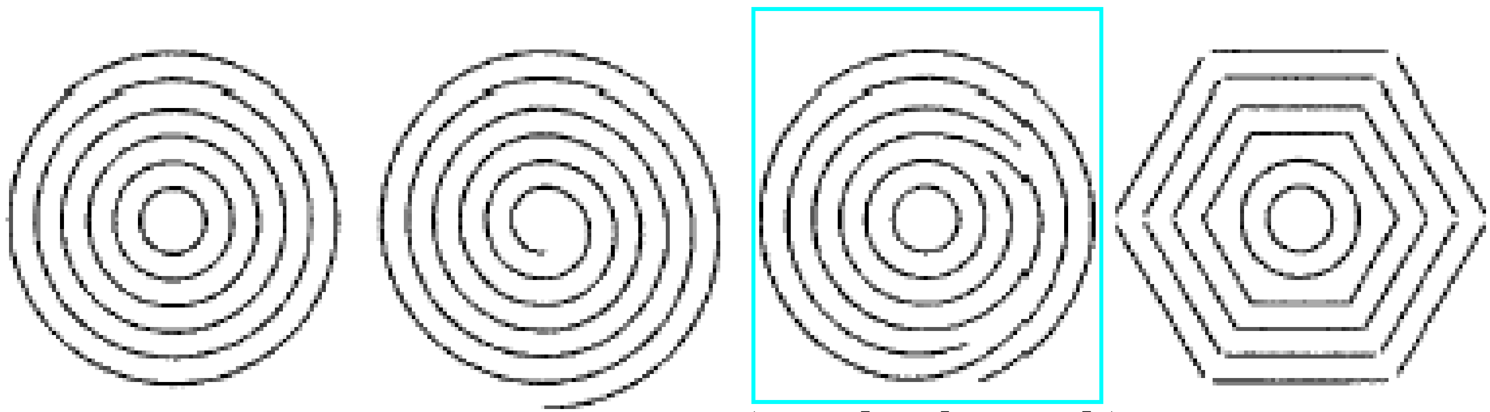
C_{20}



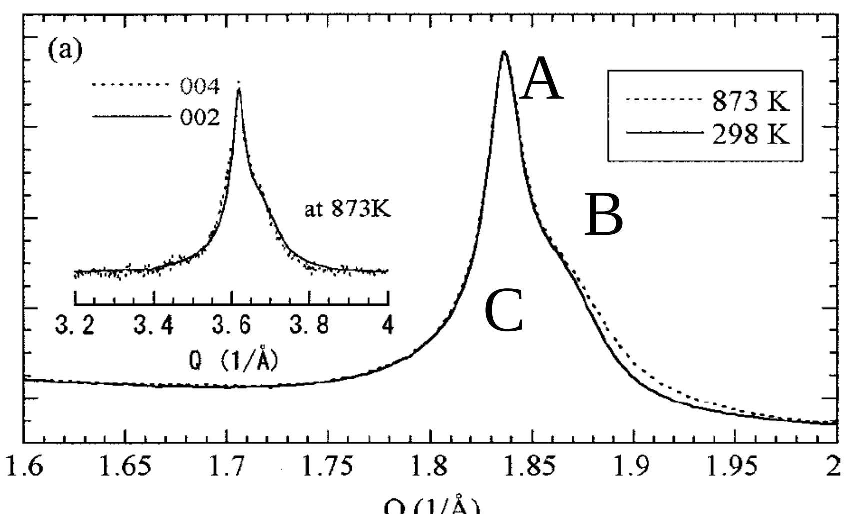
Y. Maniwa et al, *PRB* **64**(2001)073105.

An XRD study on MWNTs (Arc discharge, H_2, No metal)

Thin MWNTs: “Concentric (Russian doll)” type
Thick MWNTs: “Scroll” and/or “Concentric” , “Polygonal”



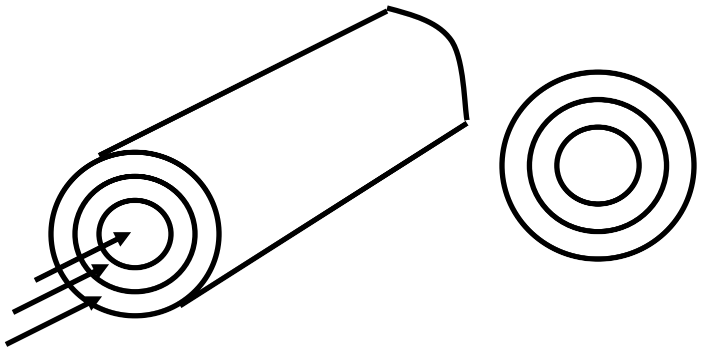
(Amelinckx et al.)



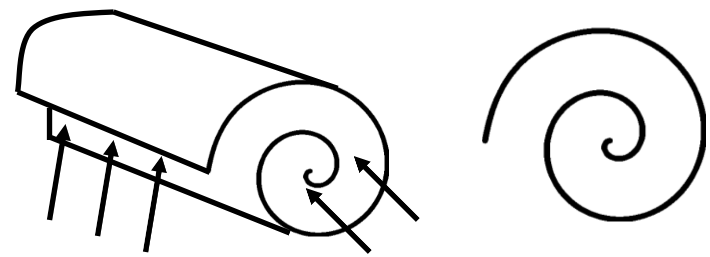
Thermal-expansion coefficients

A: 2.6 x 10^{-5} K^{-1} (graphitic impurity)
B: 2.5 x 10^{-5} K^{-1} (jelly role parts)
C: 1.6 x 10^{-5} K^{-1} (concentric parts)

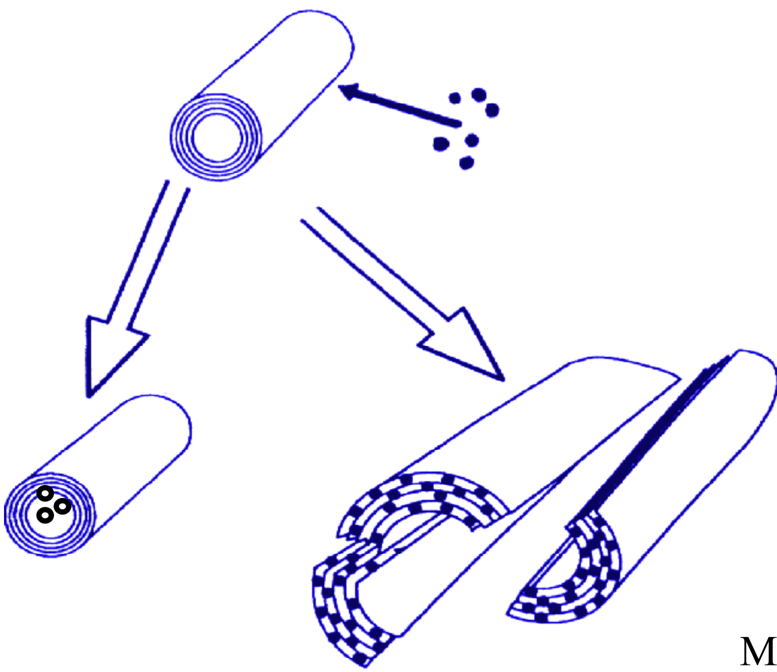
Structures of Multi-Wall Carbon Nanotubes

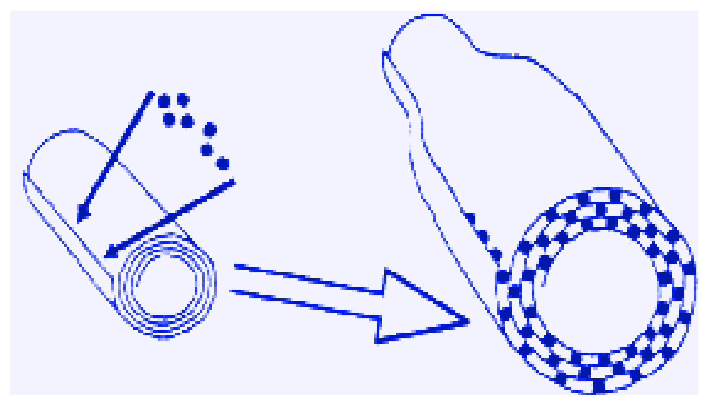


Russian-doll type
(CCVD)



Scroll type
(Arc discharge without
metal catalysts ?)



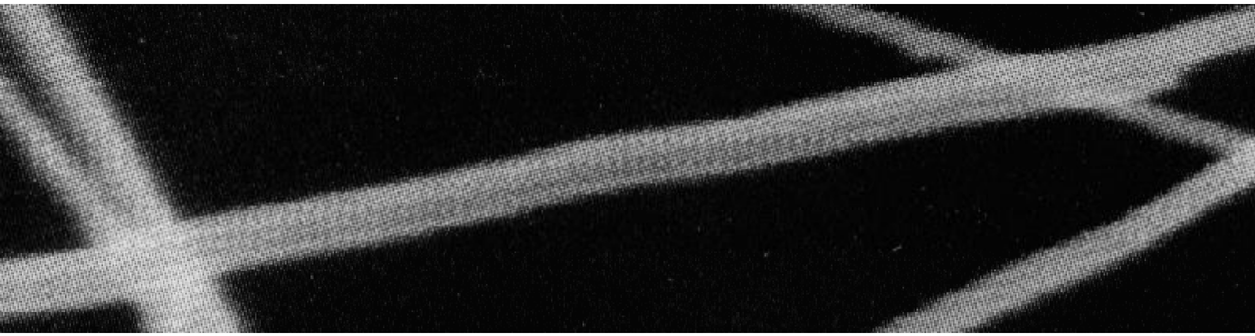


Mordkovich et al. “Supercarbon” (Eds. Yoshimura, Chang)
Springer, 1998, p.107.

020119a

Intercalation is possible for scroll-type MWNTs

Mordkovich et al. "Supercarbon" (Eds. Yoshimura, Chang) Springer, 1998, p.107.



300 nm

Intercalation of $FeCl_3$ into scroll-type MWNTs

Left in air for 1 week and washed with water.