化学気相成長(CVD)法による カーボン薄膜の成長制御

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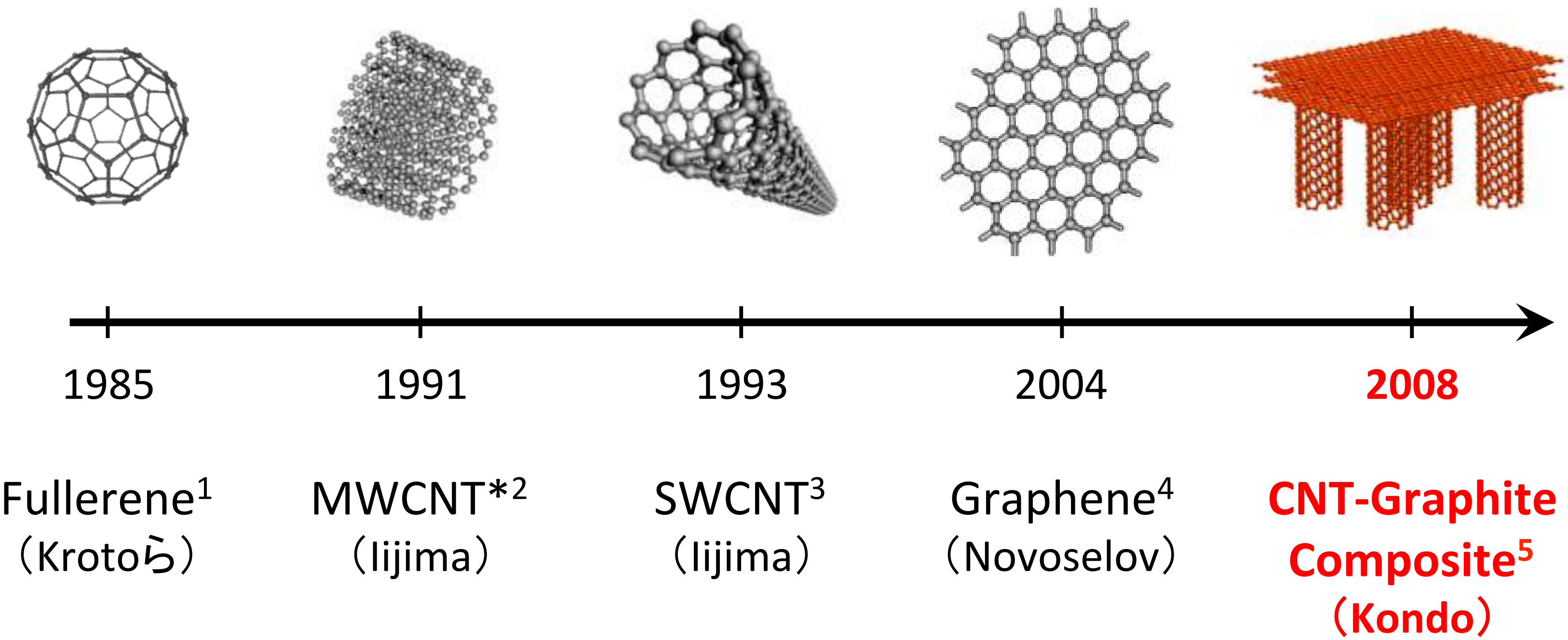
1. カーボンナノチューブーグラフェン複合体
2. グラフェン

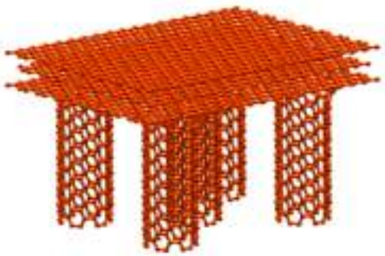
Discovery of Nano Carbons



* CNT: carbon nanotube

(1) H. W. Kroto et al., Nature, **318** (1985) 162. (2) S. Iijima, Nature, **354** (1991) 56.
(3) S. Iijima and T. Ichihashi, Nature, **363** (1993) 603. (4) K. S. Novoselov et al., Science, **306** (2004) 666.
(5) D. Kondo et al., Appl. Phys. Express, **1** (2008) 074003.

Physical Properties

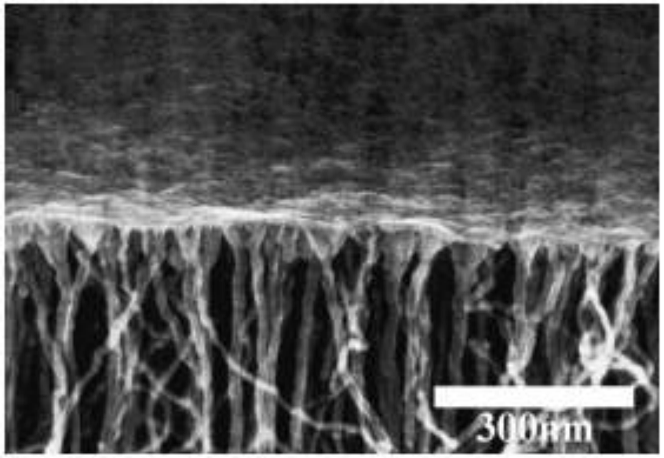


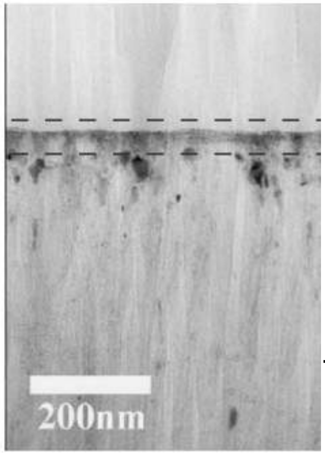
Materials	E cond S/m	current A/cm^2	Ther cond W/(m K)
Graphene	10^8	10^8	~5000
SWCNT	10^6–10^7	10^9	~3500
MWCNT	10^4	–	~3000
Silver	6.8×10^7	–	428
Copper	6.5×10^7	10^6	403
Aluminum	4.0×10^7	–	236

- Excellent electric and thermal conductivity properties of the composite, consisting of graphenes and carbon nanotubes are expected

Application: Via-hole wiring of electronic circuitry, etc

Composite structure first revealed by Kondo[5]

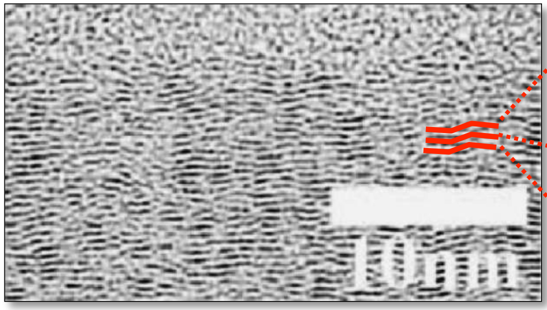


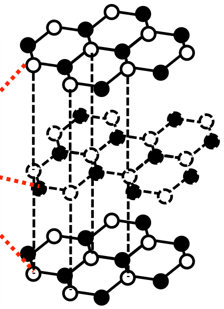


Scanning Electron Microscope

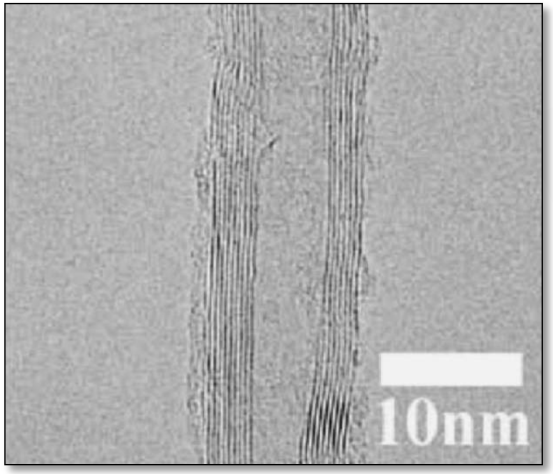
Transmission Electron Microscope

Graphene layer[5]





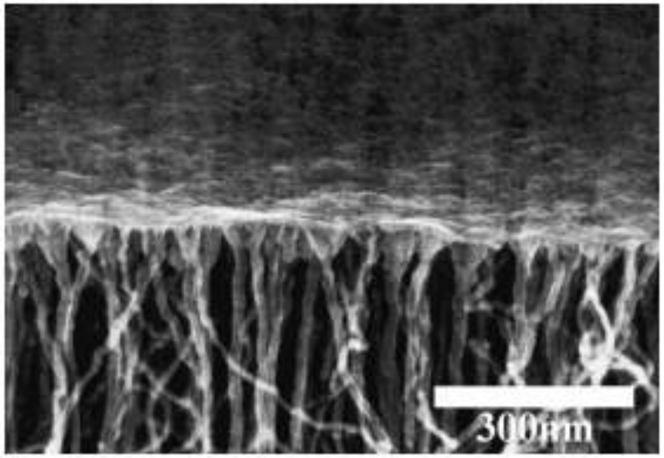
MWCNT[5]



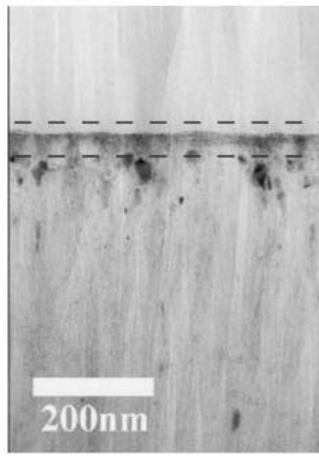
(5) D. Kondo et al., Appl. Phys. Express, **1** (2008) 074003.

*SEM: scanning electron microscopy **TEM: transmission electron microscopy

Composite structure revealed by Kondo[5]

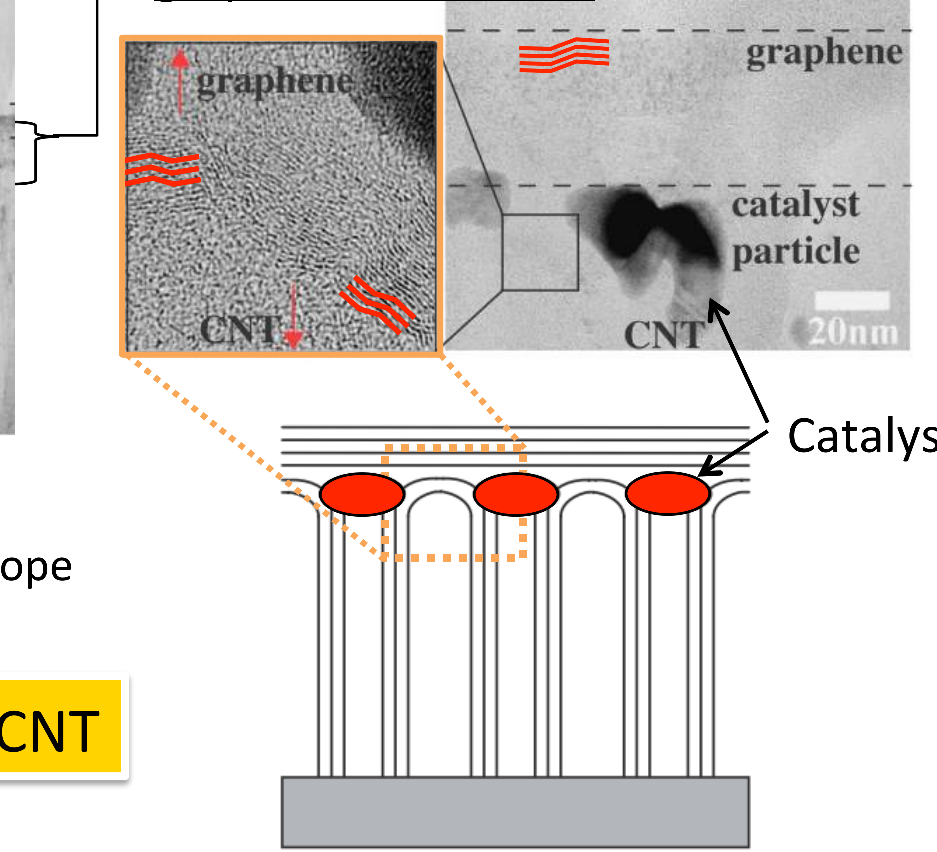


Scanning Electron Microscope



Transmission Electron Microscope

Interface between surface graphene and CNTs[5]



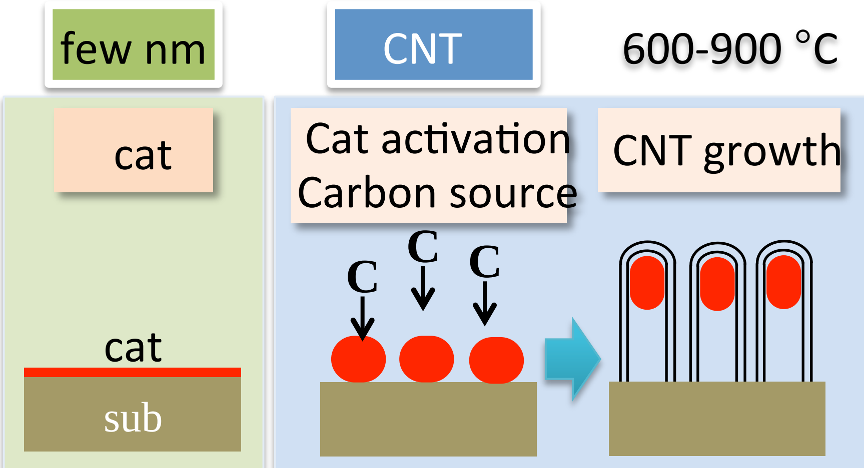
Model of composite by Kondo[5]

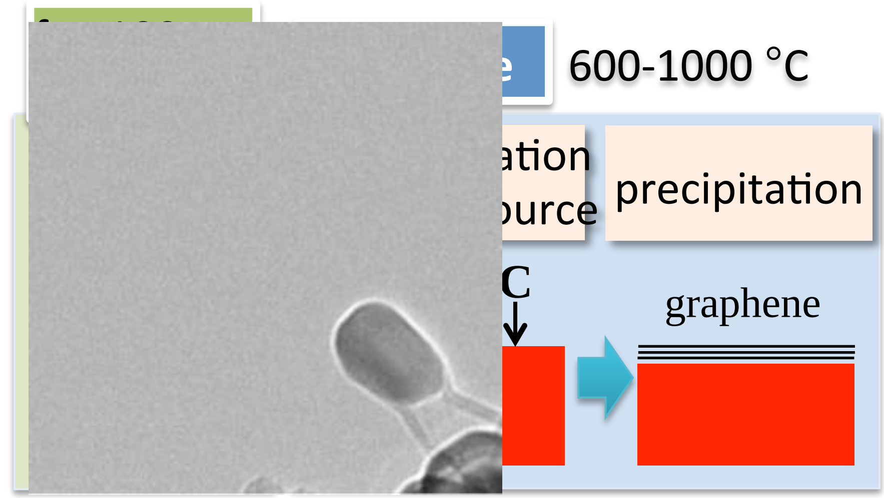
Catalyst particles on the tip of CNT

(5) D. Kondo et al., Appl. Phys. Express, **1** (2008) 074003.

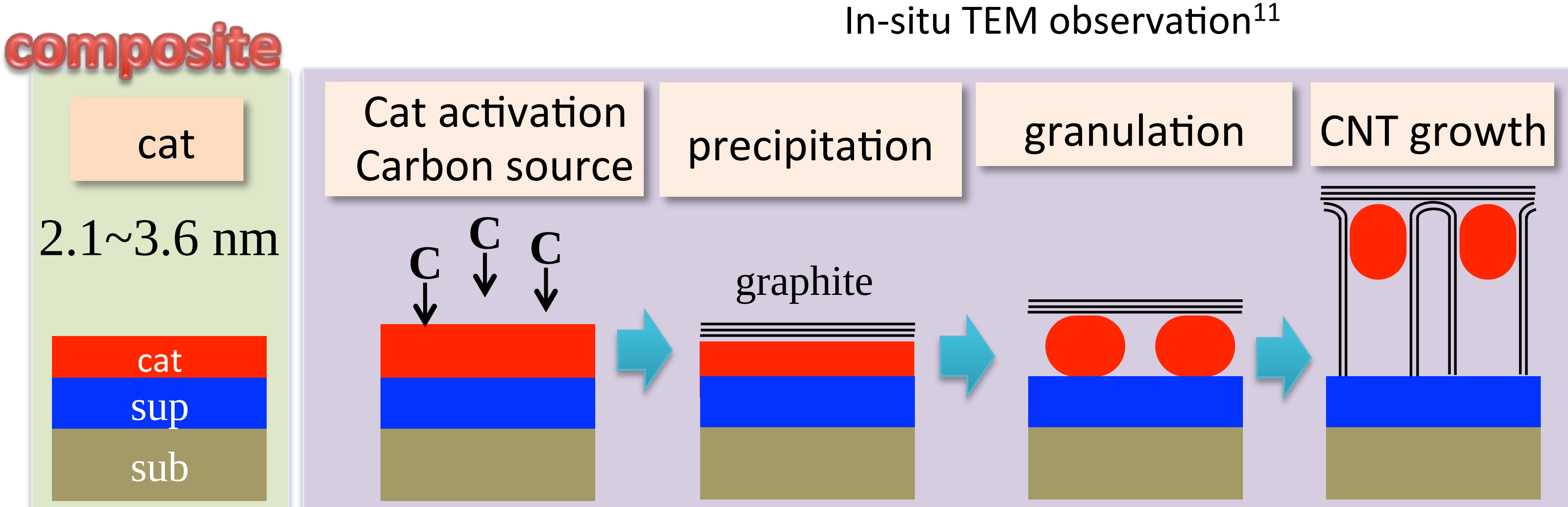
*SEM: scanning electron microscopy **TEM: transmission electron microscopy

CVD growth of carbon films





In-situ TEM observation[11]

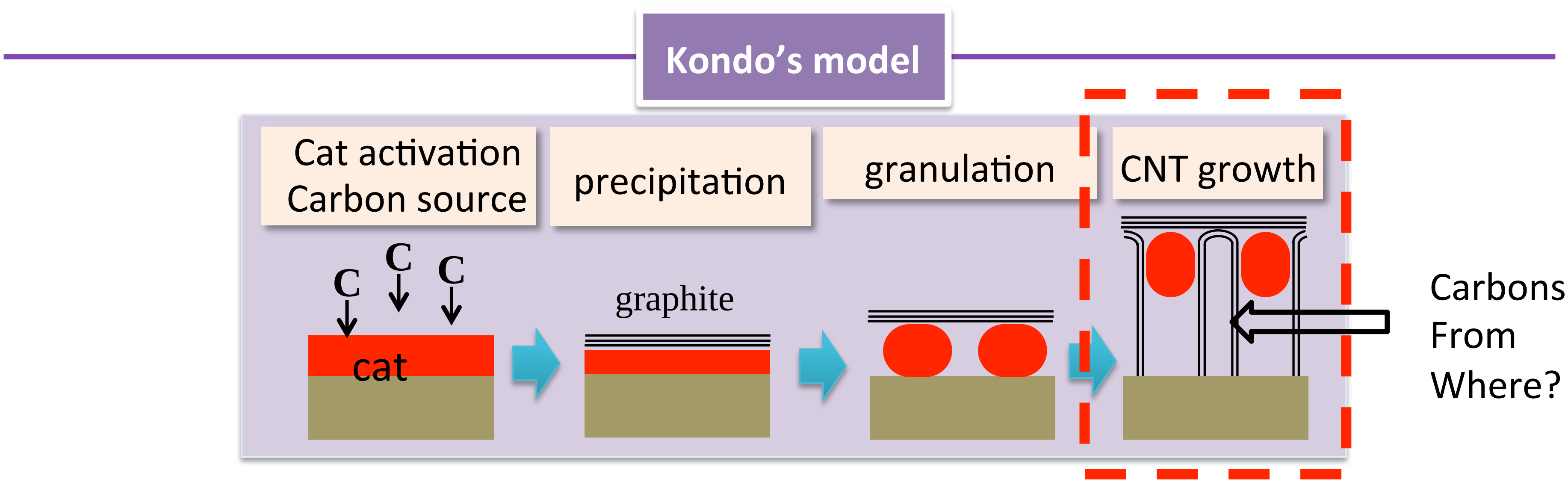


(5) D. Kondo et al., Appl. Phys. Express, **1** (2008) 074003.

Question about the previous model

How is carbon supplied into the catalyst under the graphite layers?

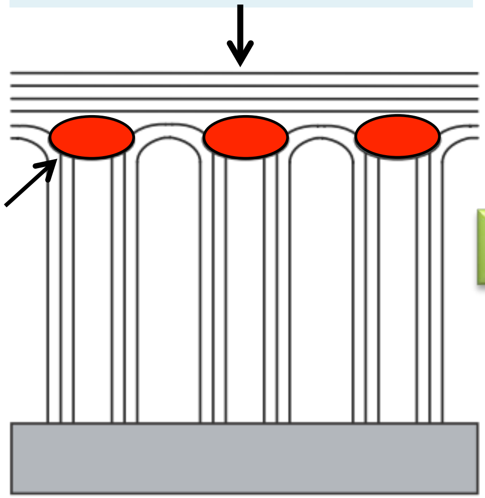
- In the Kondo's model, the catalyst is covered with graphite and CNTs
- Catalyst loses its activity when covered with amorphous carbon or graphite[13]



(13) K. Hata et al., Science **306** (2004) 1362.

Ideal vs. Real Structure

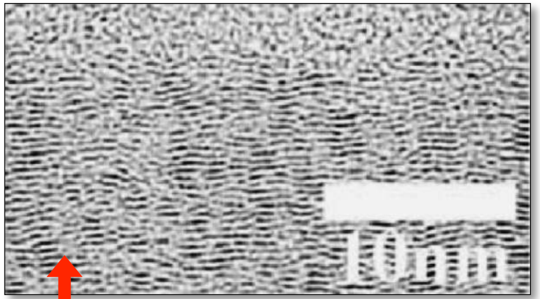
Flat, higher Ordered Graphite



cat

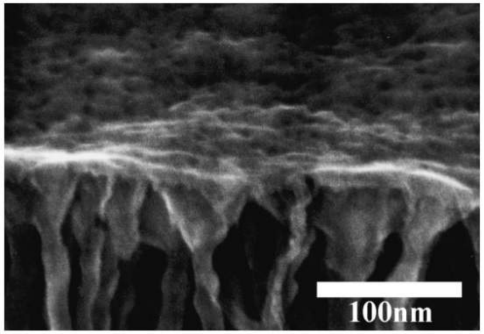
Model proposed by Kondo[5]

Surface Graphite Layers[5]

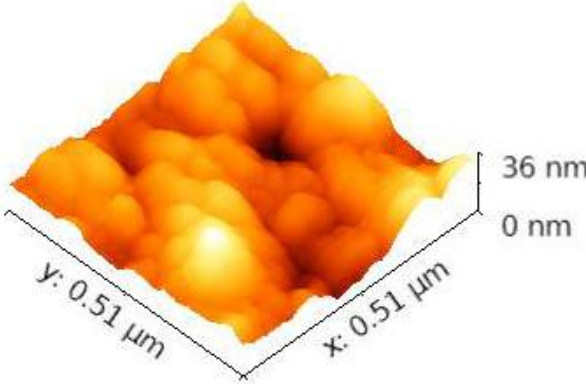


Noncontinuous (turbostratic)

Structure of Surface Graphite



SEM by Kondo



Our AFM image

Rough particle-like morphology

(5) D. Kondo et al., Appl. Phys. Express, **1** (2008) 074003.

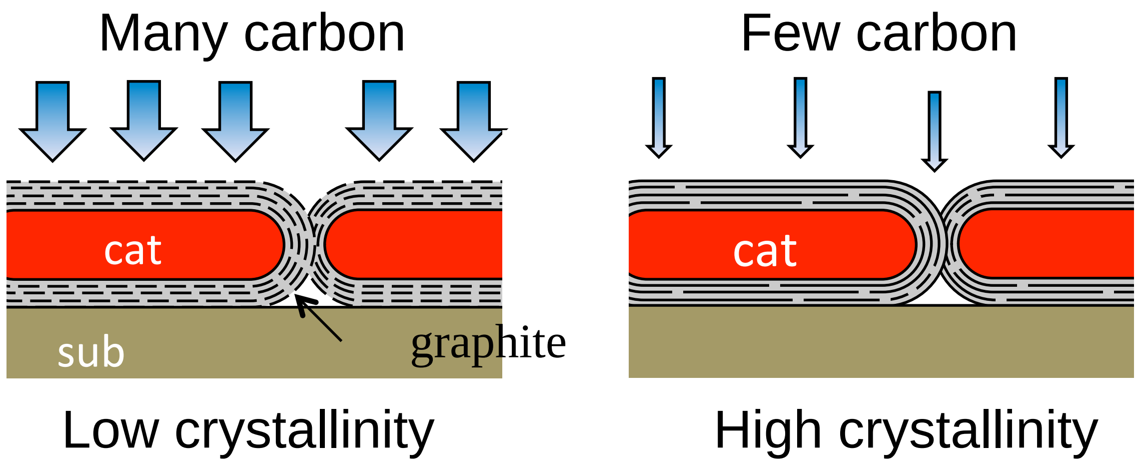
* AFM: atomic force microscopy

Effect of Catalyst Materials (Fe, Co)

How carbon atoms go into the surface graphite layer?

assumption : Defects in the graphite layers have role as a path.

Initial growth of composite



- The crystal quality of surface graphite layers supposed to affect the growth of composite

Effect of Catalyst Materials (Fe, Co)

How the carbon go into the surface graphite layer?

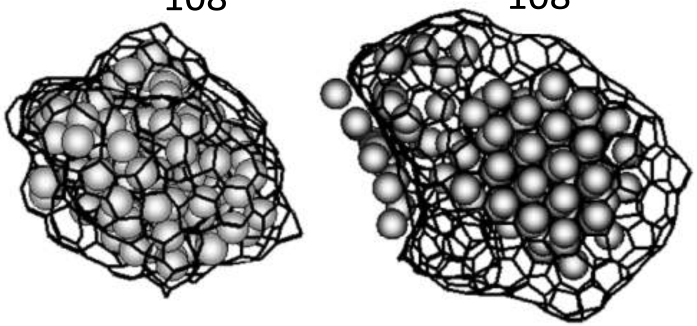
assumption : defects in the graphite layers have role

The purpose:

- To clarify the carbon supply path into the underlying layers
- To clarify the growth model of composites

✓ Crystallinity of precipitated carbon[20]
  - Fe: five- and seven-membered rings
  - Co : high quality

➢ Comparison between Fe and Co catalyst



Graphite precipitation[20]
(Shibuta's simulation)

(20) Y. Shibuta and S. Maruyama, Comp. Mater. Sci., **39** (2007) 842.

Experiment

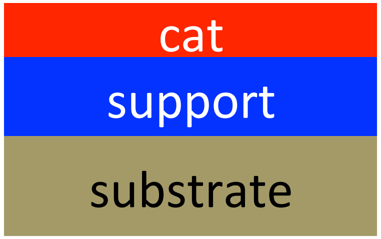
☐ <u>Substrate</u>

- SiO_2(50 nm)/Si

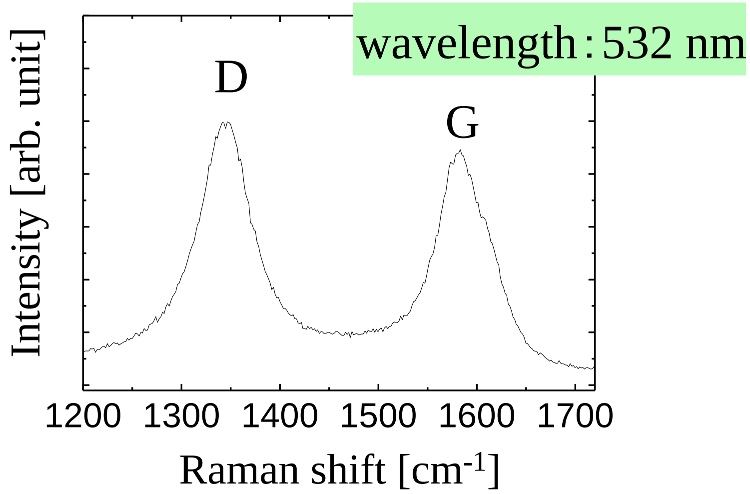
- **Supporting layers**: Al_2O_3
  RF-sputterig（Al_2O_3 target）

- **catalyst**: **Fe, Co**
  – Arc-plasma deposition

※ thickness measurement by AFM
（precision： ±0.1 nm）



Raman Spectroscopy



D: defect-related peak, G: graphite peak

I_G/I_D: estimate of crystallinity

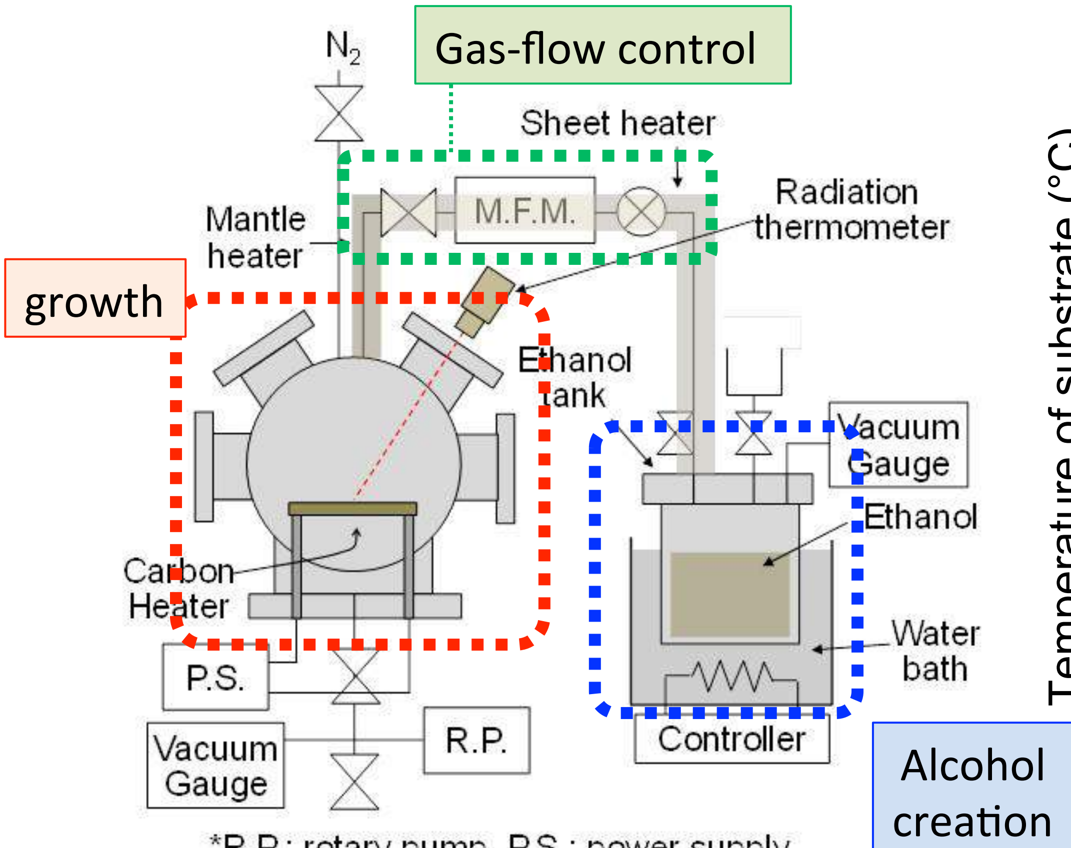
M. S. Dresselhaus et al., Phys. Rep., **409** (2005) 47.

☐ Alcohol thermal Chemical Vapor Deposition (CVD)

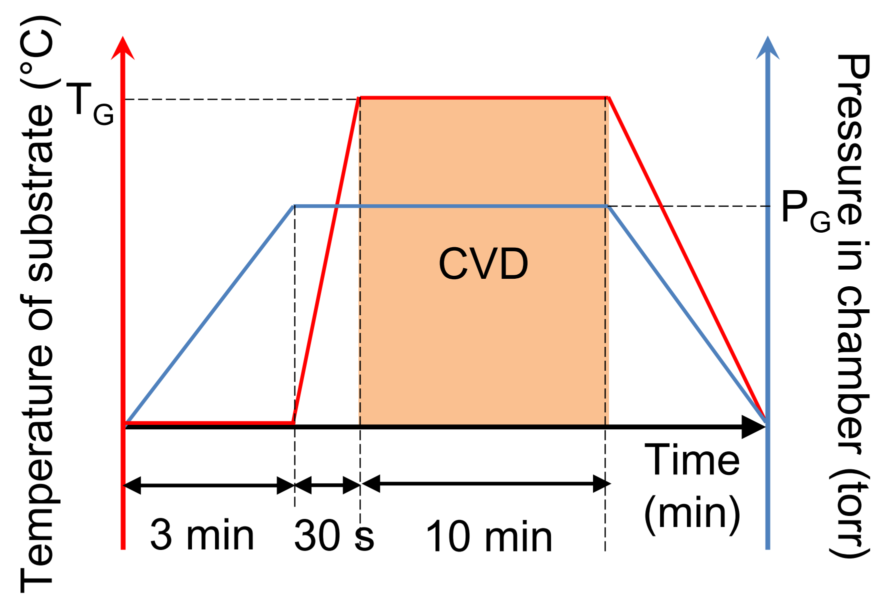
- Carbon source :　alcohol（ethanol）

※C_2H_2 has been previously used

- **Custom-made apparatus**

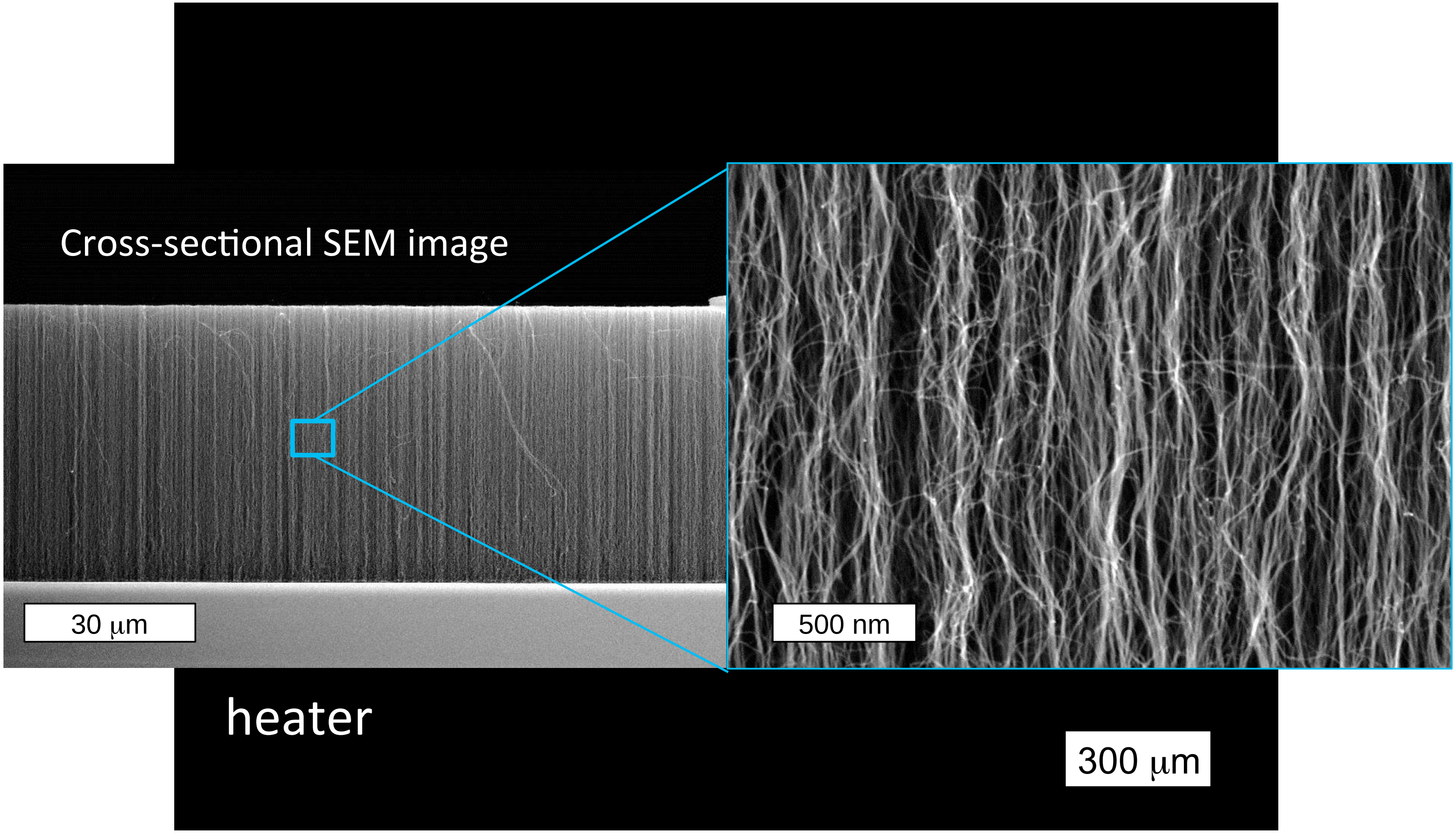


*R.P.: rotary pump, P.S.: power supply, M.F.M.: mass flow meter



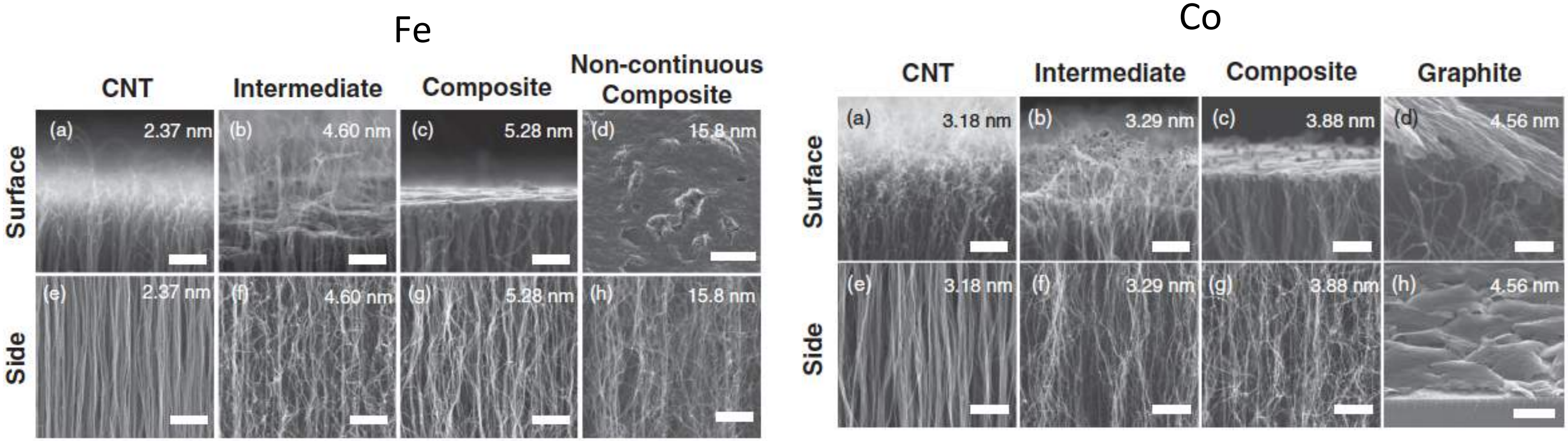
T_G: growth temperature (670°C)
P_G: growth pressure (150 torr)

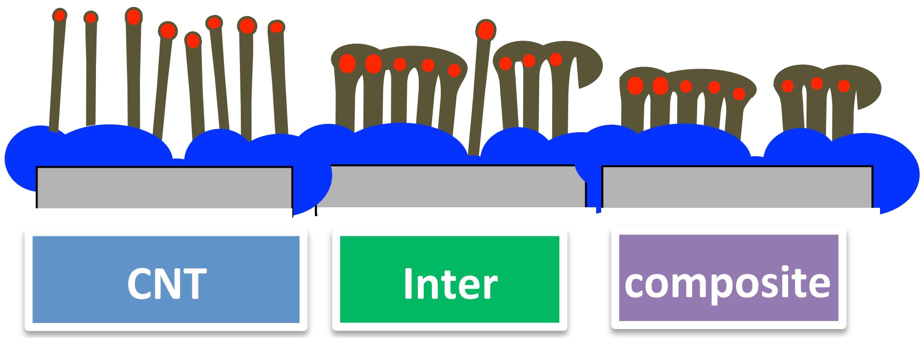
- CVD growth of CNT by Alcohol CVD



* cat: Co, thickness: 2.0 nm, Temp 800C, Pressure 310 torr, 5 min growth

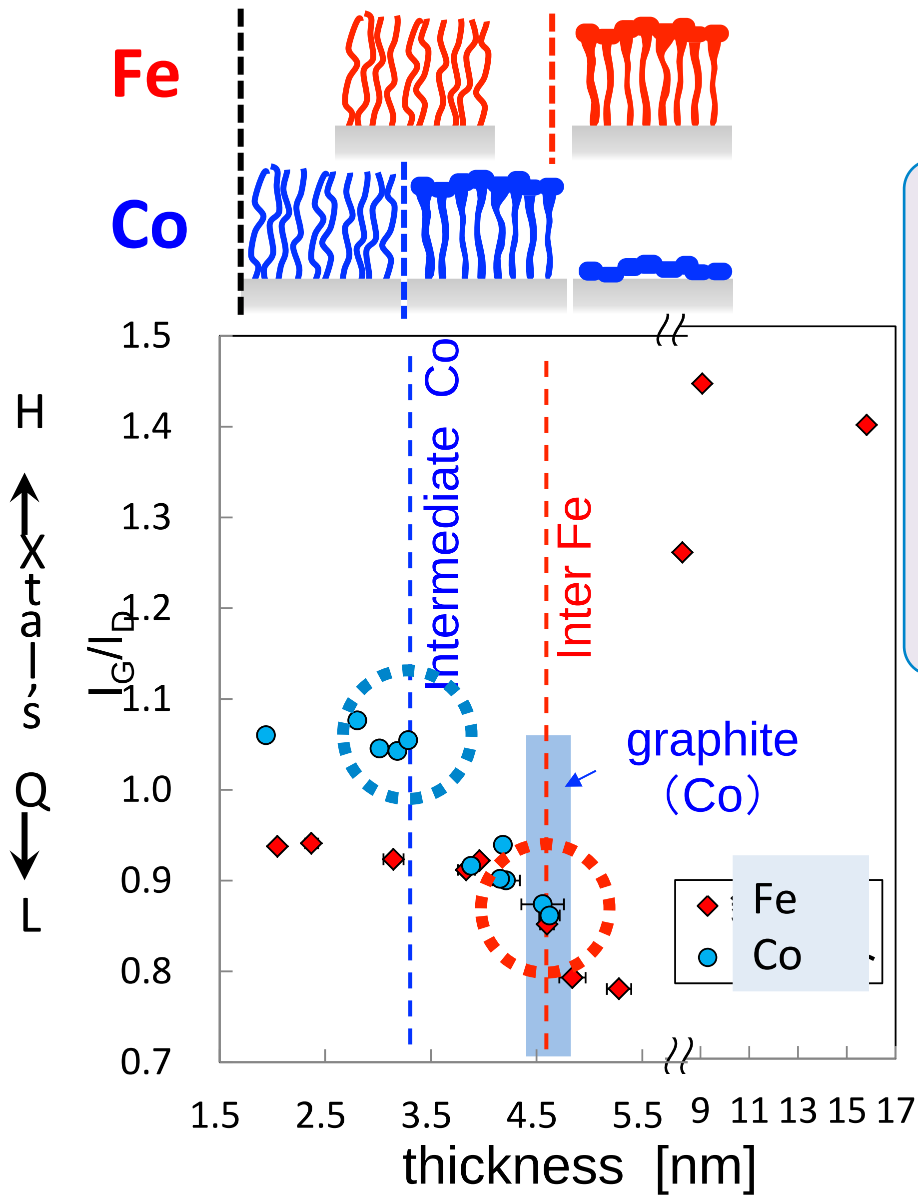
Growth of Carbon Films from Fe and Co





- Composite growth at thinner region for Co than Fe
- Graphite formation at thick Co

Crystallinity of composites grown from Fe and Co

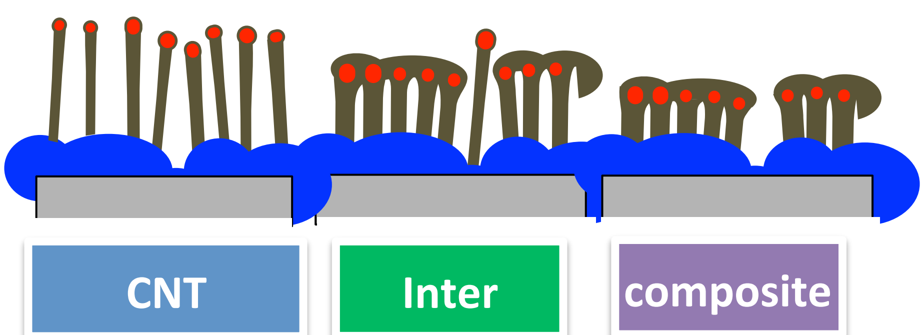


- Crystallinity : Raman (I_G/I_D)

Fe (0.79) < Co (1.05)

✓ Consistent with the Shibuta's study

Co precipitates higher quality of graphenes

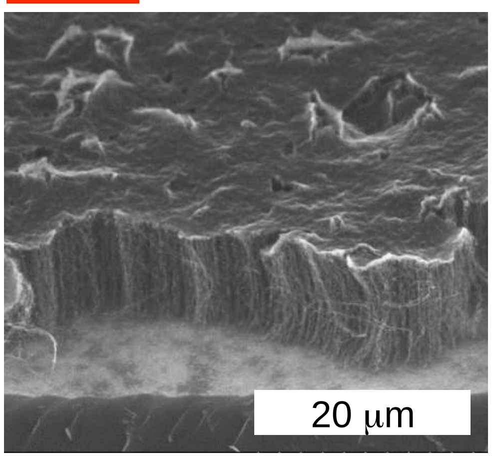


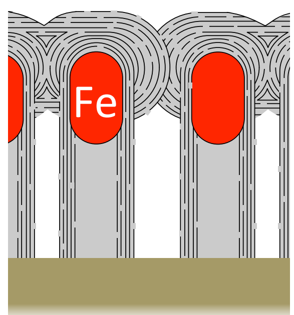
Effect of Catalyst Materials (Fe, Co)

Growth at thick catalyst region

- CNT arrays under the graphite for Fe
- No CNT arrays under the graphite for Co

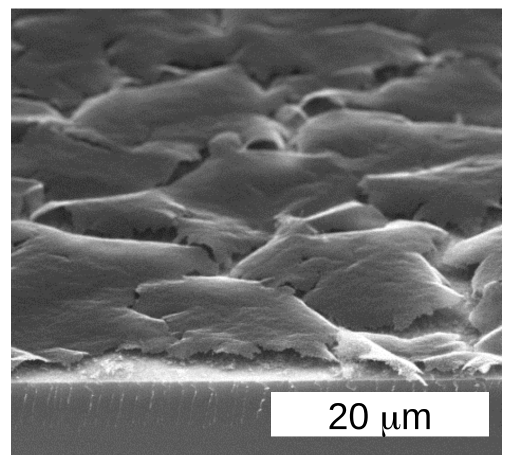
Fe 15.8 nm

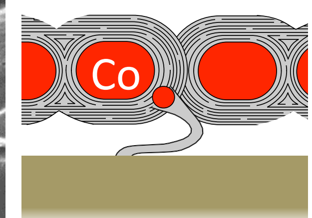




Composite formation

Co 4.6 nm





Graphite formation

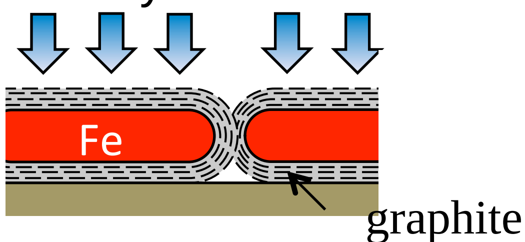
Effect of Catalyst Materials (Fe, Co)

Defect in Graphite is path or not?

Fe : composite ⟷ **Co** : graphite

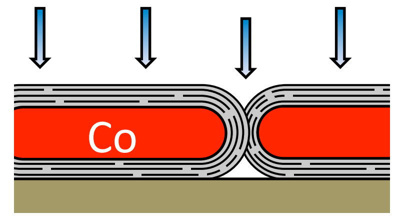
Initial stage

Many Carbon

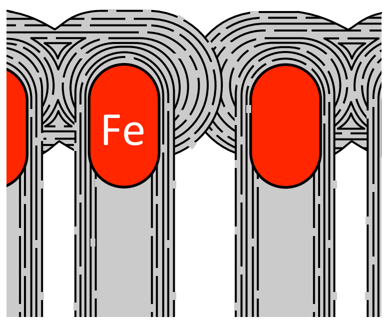


Low crystallinity

Few carbon

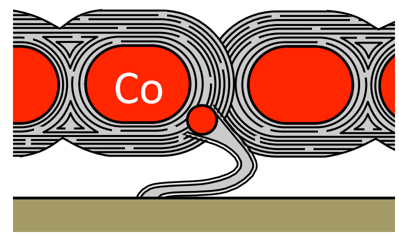


High crystallinity



CNT growth

composite

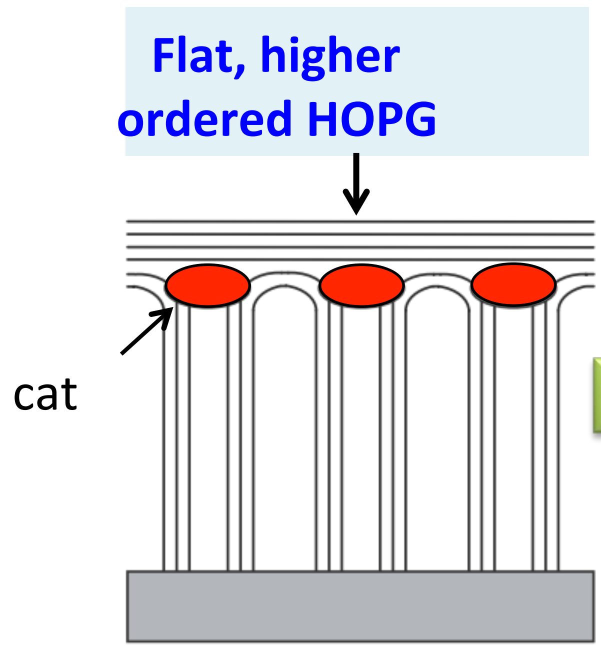


No CNT

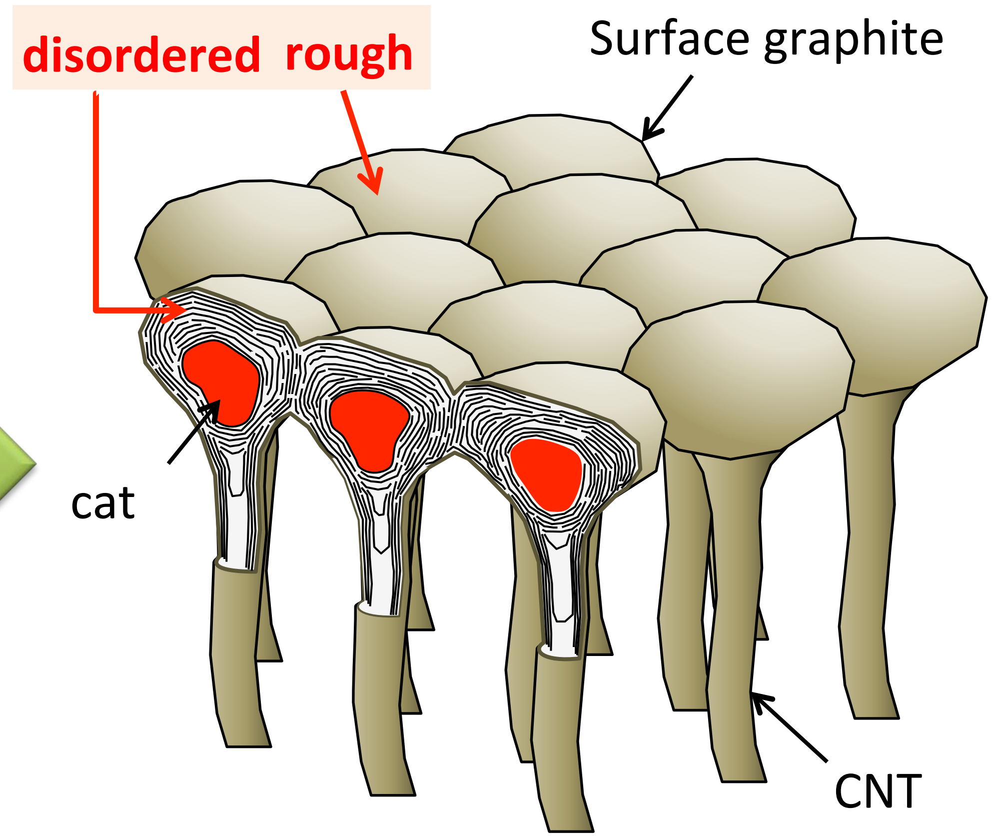
graphite

Graphite defects is PATH of carbons

Real Structure of the composites



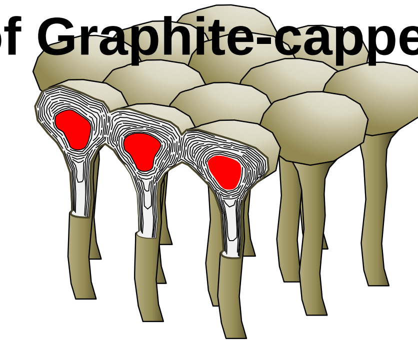
Model proposed by Kondo[5]



Our proposed structure

Conclusions

☐ Effect of Catalytic Material to the Synthesis of Graphite-capped Vertically Aligned Carbon Nanotube Arrays

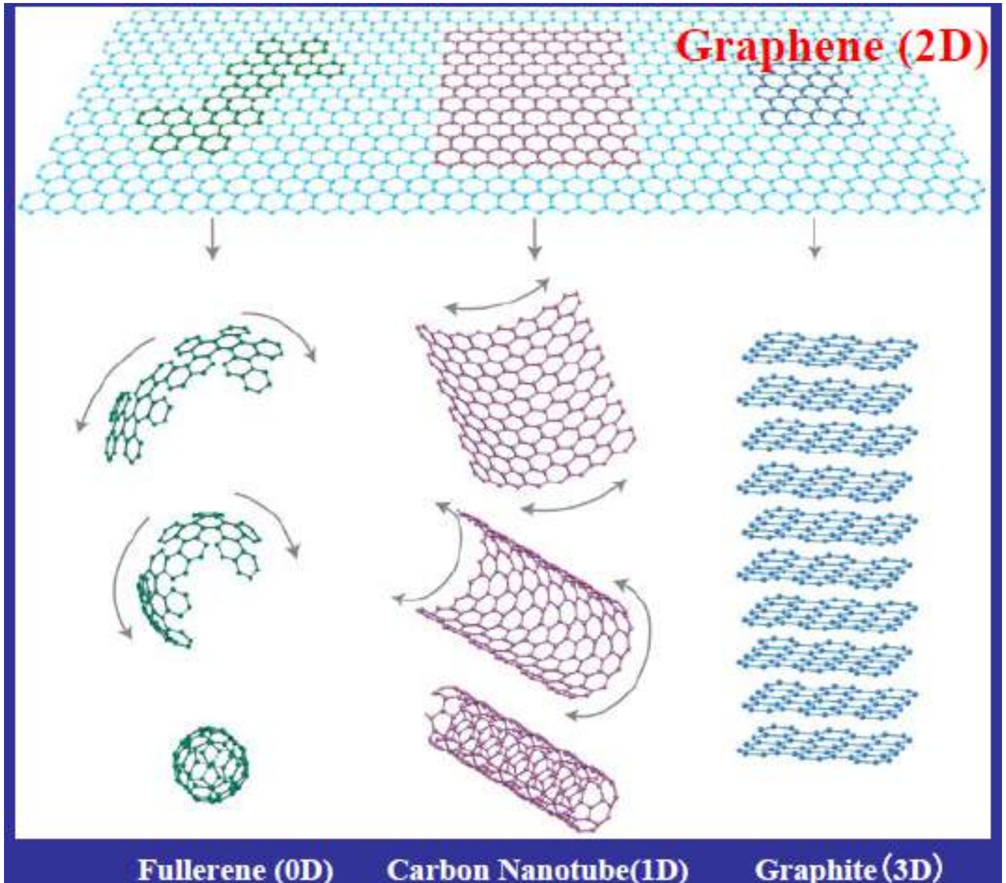


- Iron catalyzed aligned CNT arrays at the overall thickness (2.0 ~ 15.8 nm for CNT arrays ~ composite), while cobalt catalyst lost its activity to synthesize aligned CNT arrays above 4.6 nm.
- Crystallinities of the CNTs arrays synthesized from thin iron and cobalt film were compared by Raman spectroscopy. The Co–catalyzed CNTs showed better crystallinity than Fe-catalyzed ones (GD ratio: 1.05 and 0.79 for cobalt and iron, respectively).
- Based on these results, defects in the graphitic forms are assumed as paths of the carbon supply to the catalyst. Since the cobalt catalyst precipitates higher crystalline graphite than iron, the cobalt deactivates quickly because of suppression of carbon supply, resulting in the formation of graphite film.

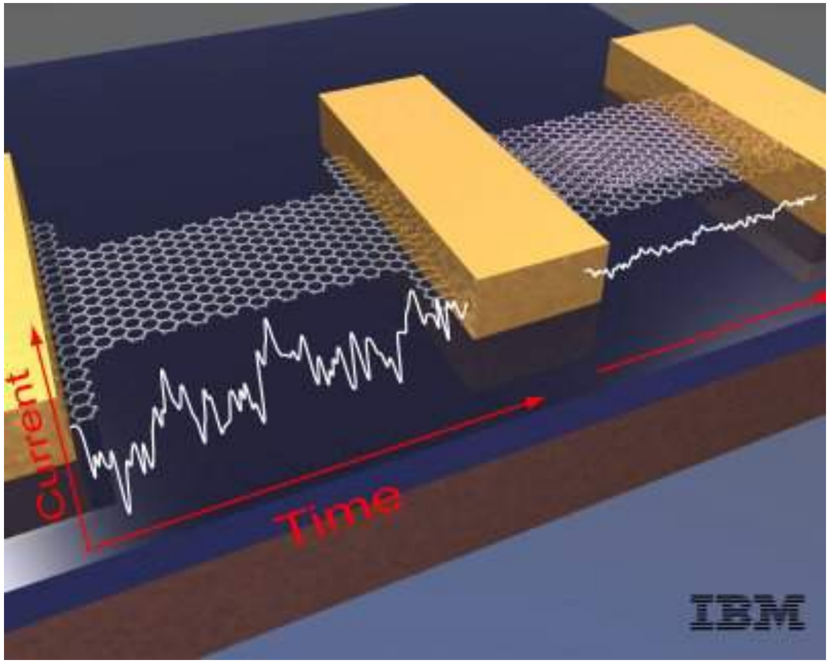
グラフェンの特性

- 高移動度(2×10^5 $cm^2/V\cdot s$)
  $1000cm^2/V\cdot s$ for Si
- 0.3μm弾道電子・スピン伝導
- 熱伝導度およびヤング率が大きい
- 高光透過率(97.7%)
- 低欠陥濃度($\sim1x10^{10}cm^{-2}$)

材料	熱伝導度 (W/cm・K)	ヤング率 (10^9Pa)
グラフェン	~50	1500
ダイアモンド	10~22	1050~1200
Si	1.4	131
Ge	0.6	103
SiC	4.1	450



A.K. Geim and K.S. Novoselov, *Nature Materials* 6, No.3, 183-191 (2007).



グラフェンのエレクトロニクスを中心とした応用

デバイス機能（基礎物理）

電子（n, p; 高移動度、零ギャップ、面配線・・・）
スピン（高スピン拡散、ジグザグエッジスピン、・・・）
光（ノン・ボルン・オッペンハイマー、・・・）
電子源（・・・）、複合材料（強度、導電性、・・）

材料（基礎物性）

作製・成長技術
（セロテープ：HOPG、熱処理：SiC，CVD）
（単層、複数層、平坦性、サイズ、・・・）
物性値制御（高移動度、高安定性
高スピン拡散、・・・・）

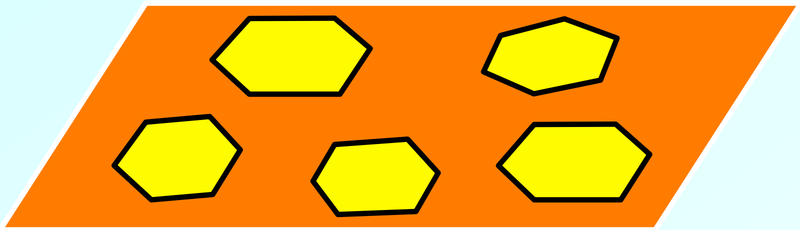
デバイス作製

単層、複数層、基板
サイズ、集積化（均一性）
エッジ構造制御、オーミック電極接合
バンドギャップ制御、ドーピング
保護膜、・・・・

ミクロな評価・高精度計測・デバイス設計理論（従来デバイスとの整合性）

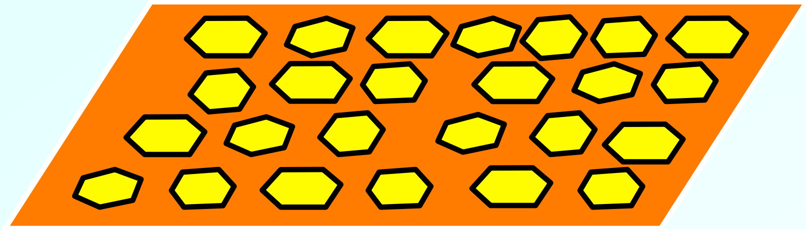
Large Size Single Crystal Domain in CVD Graphene

CVD Graphene: polycrystalline, randomly oriented



Low nucleation density

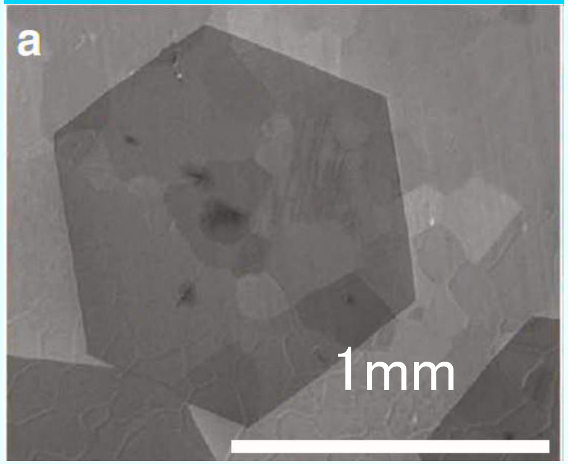
→Large domains



High nucleation density

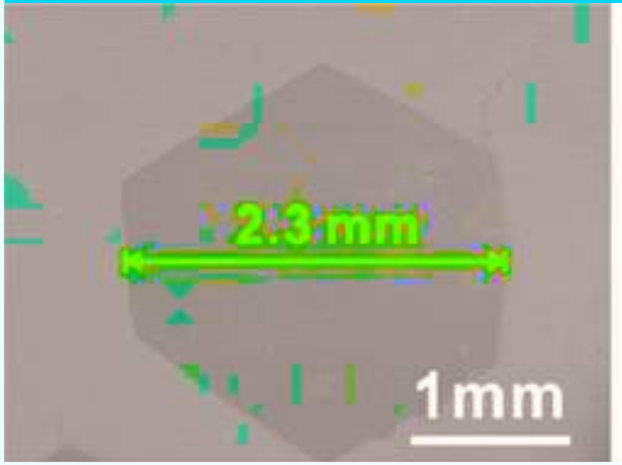
→Small domains

Graphene on Pt



L. Gao et al., Nature Commun. **3**, 699 (2012).

Graphene on Cu



Z. Yan et al., ACS Nano **6**, 9110 (2012).

Toward wafer scale graphene growth

nucleation mechanism is important

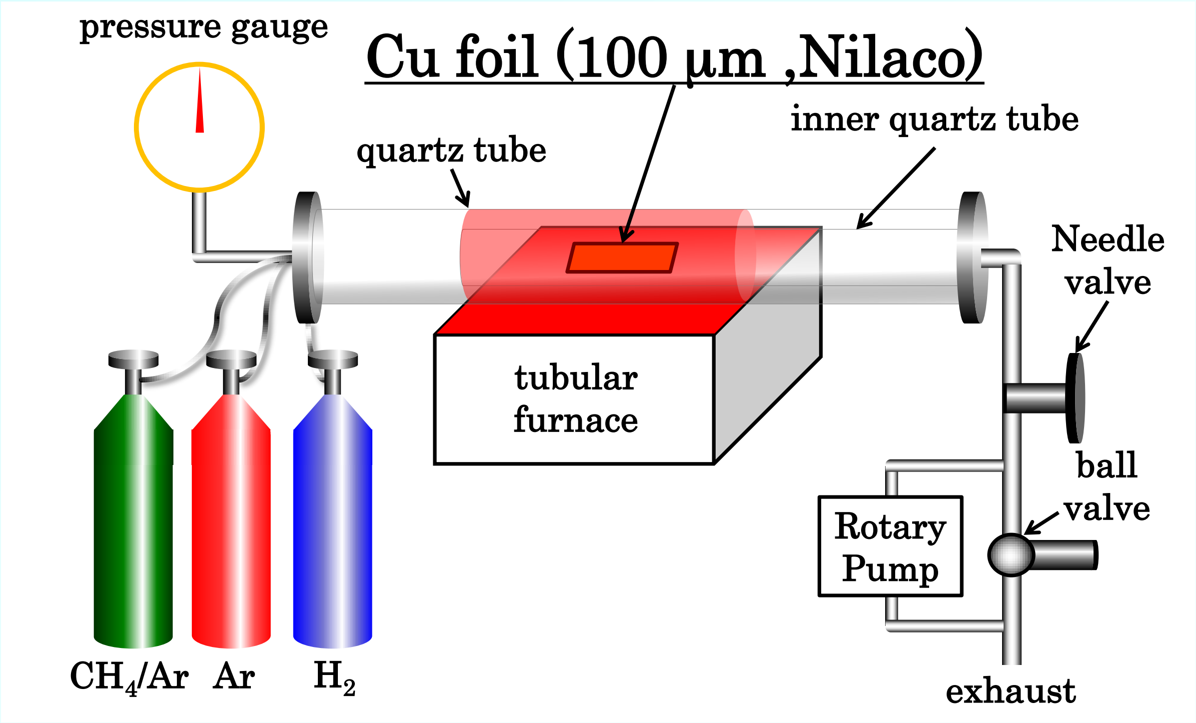
In This Talk

◆ High pressure annealing of Cu before atmospheric CVD

→ Suppress nucleation of graphene

◆ Discuss the nucleation mechanism

High Pressure Annealing and Atmospheric CVD



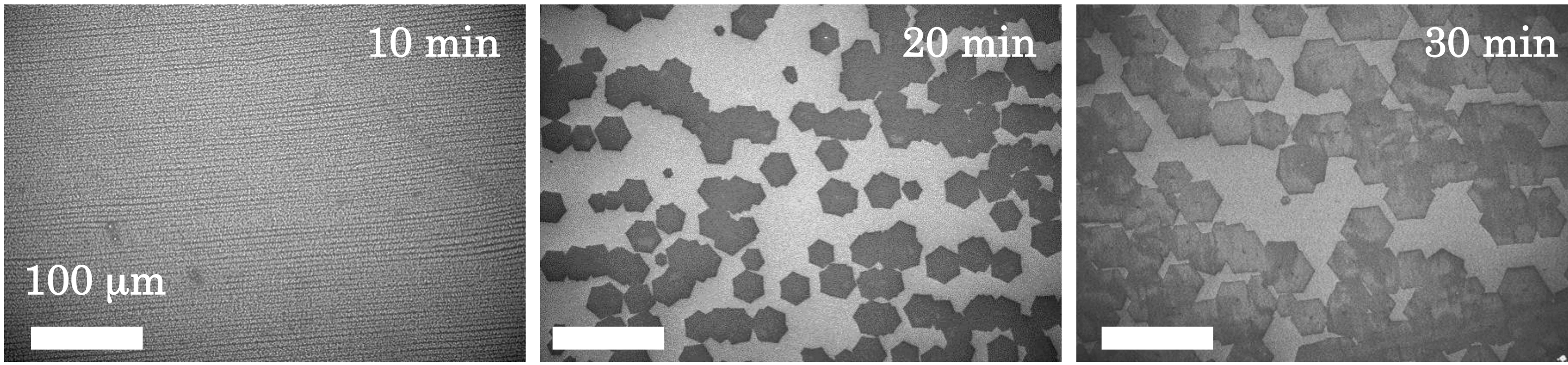
High pressure annealing ⇨ **Atmospheric CVD growth** ⇨ **Observation**
- SEM, AFM, Auger mapping

~0.34 MPa, 1050 °C
H_2/Ar, 5 h

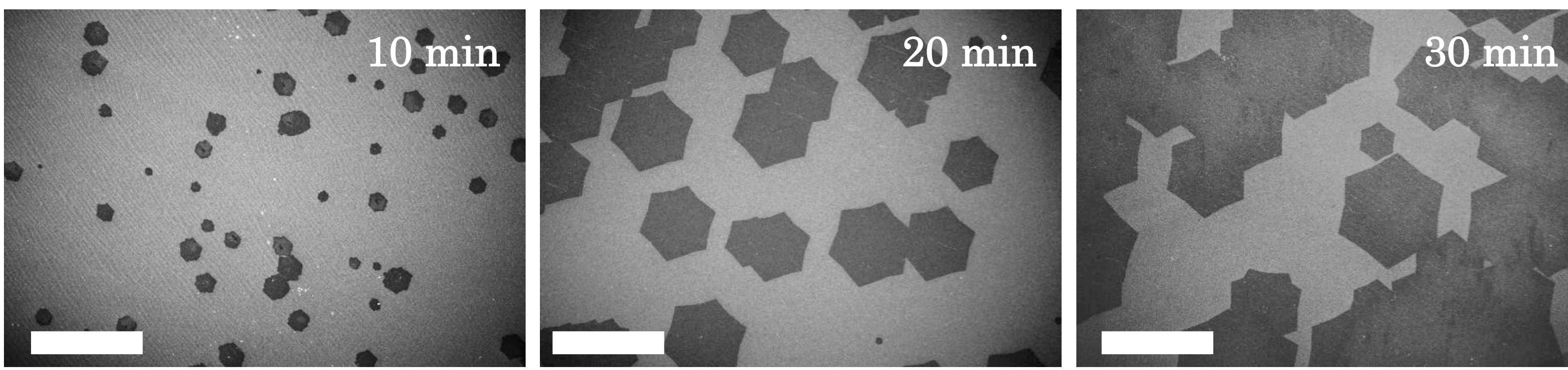
ATM, 1050 °C
H_2/Ar/CH_4(10 ppm)

SEM Observation of Graphene on Cu

Atmospheric Pressure Annealing

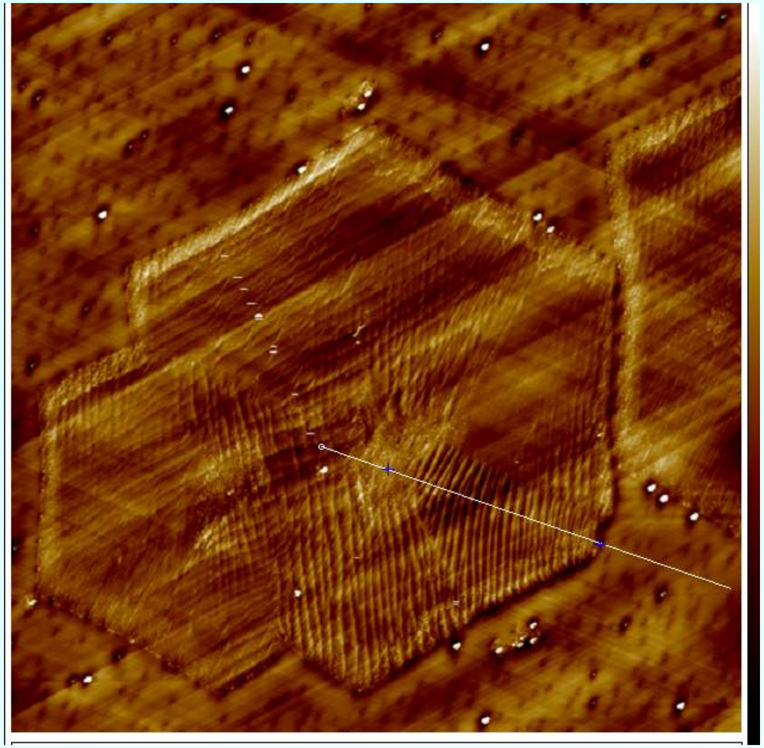


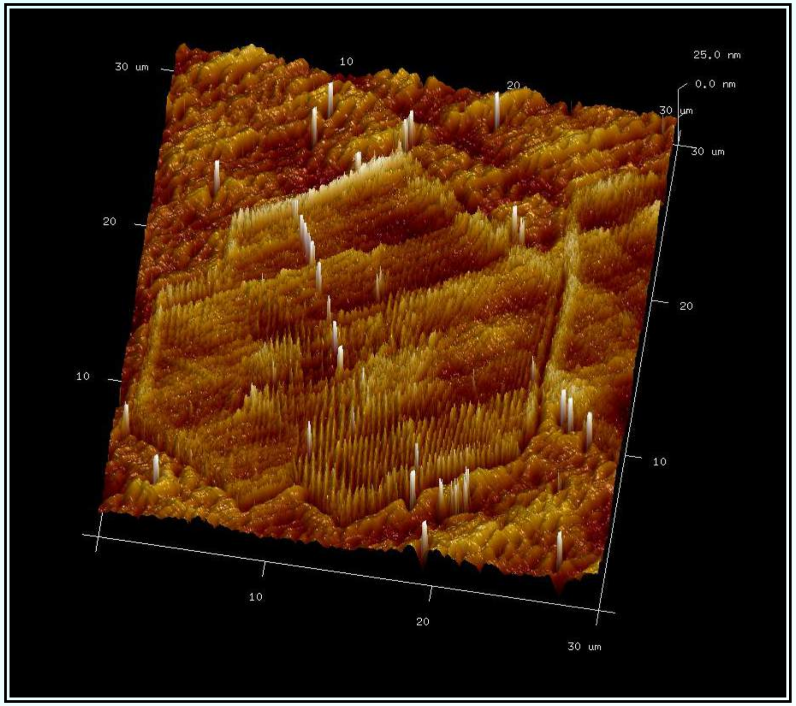
High Pressure Annealing



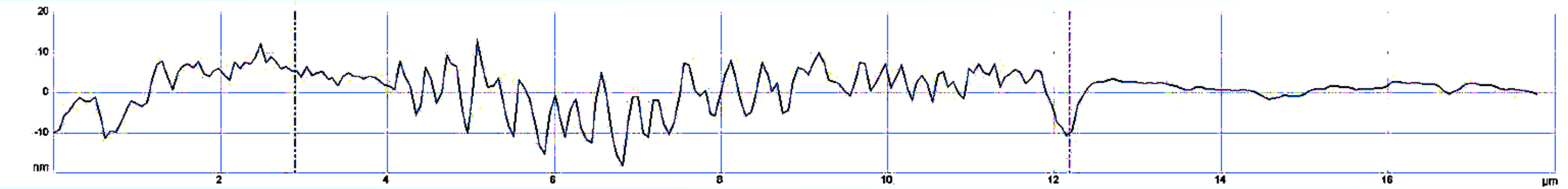
Low nucleation density on high pressure (HP) annealed Cu

AFM: #240 Graphene/Cu <Threefold Annealing>



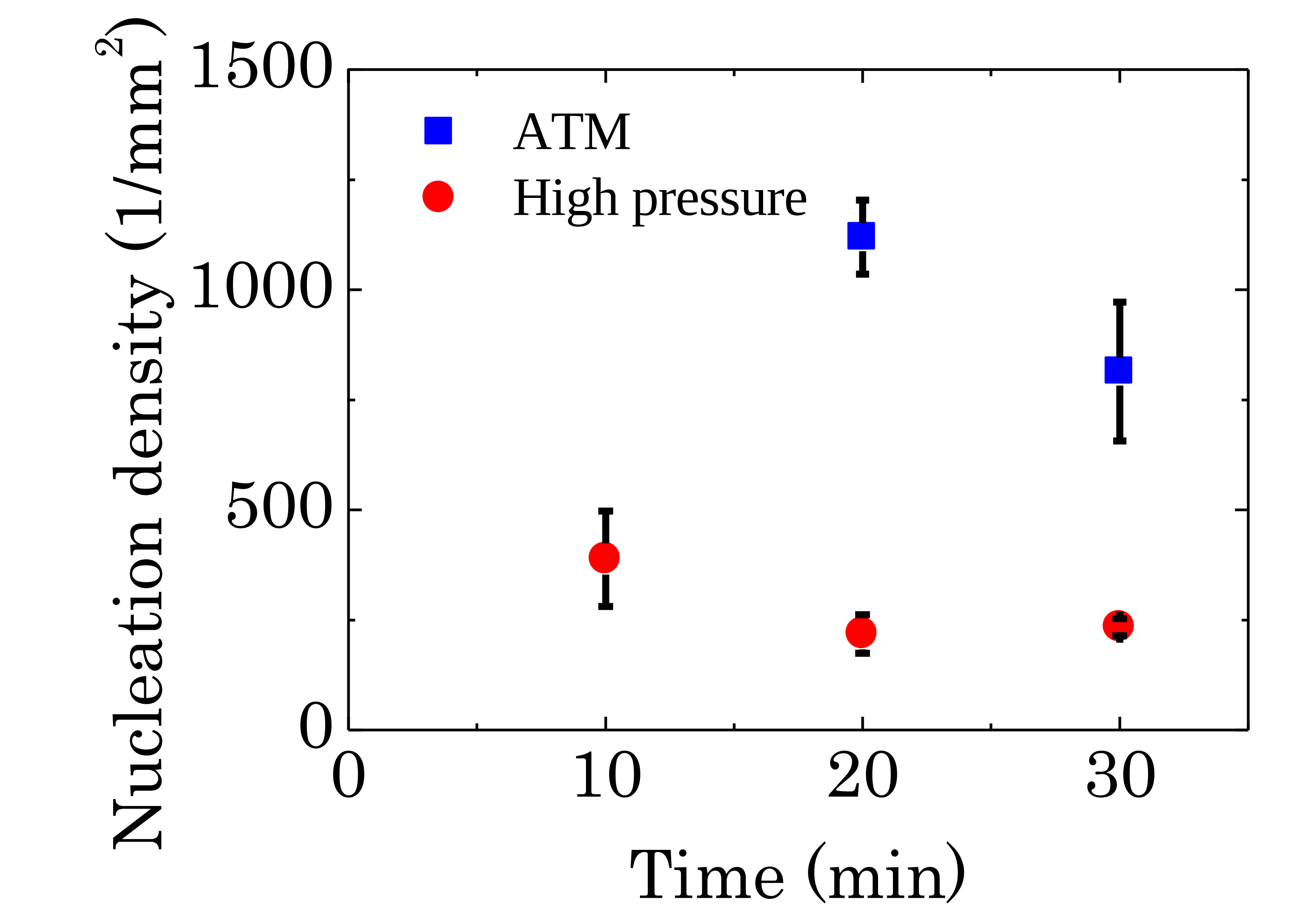


20 um



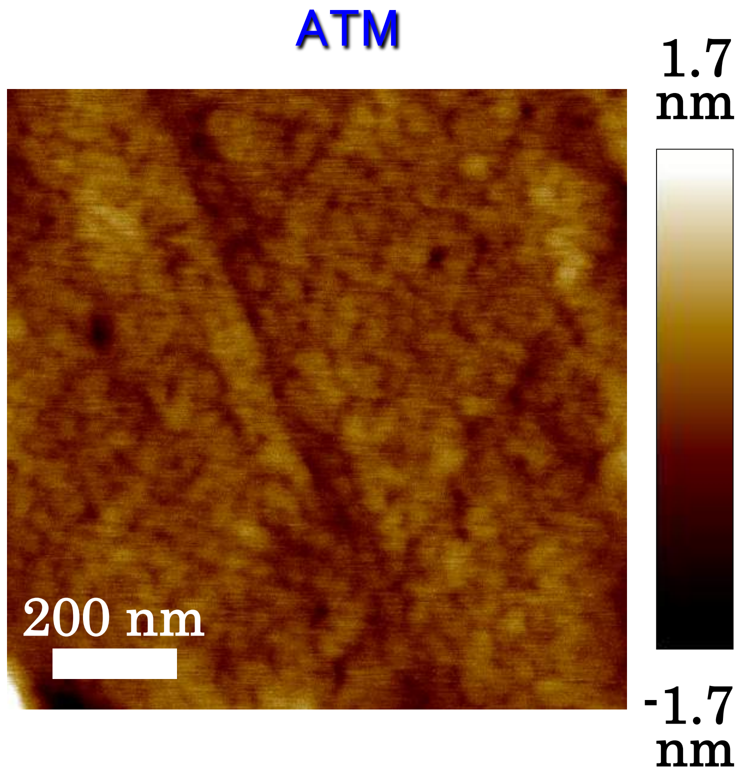
−20 um

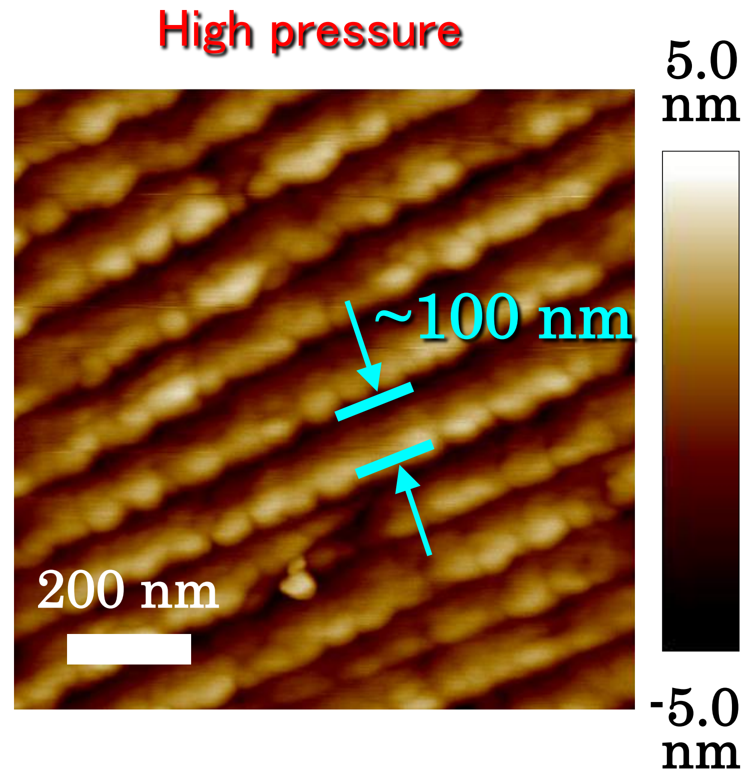
High Pressure Annealing Reduced the Nucleation



3 times lower nucleation density on HP Cu

AFM Images of the Pretreated Cu Before Growth

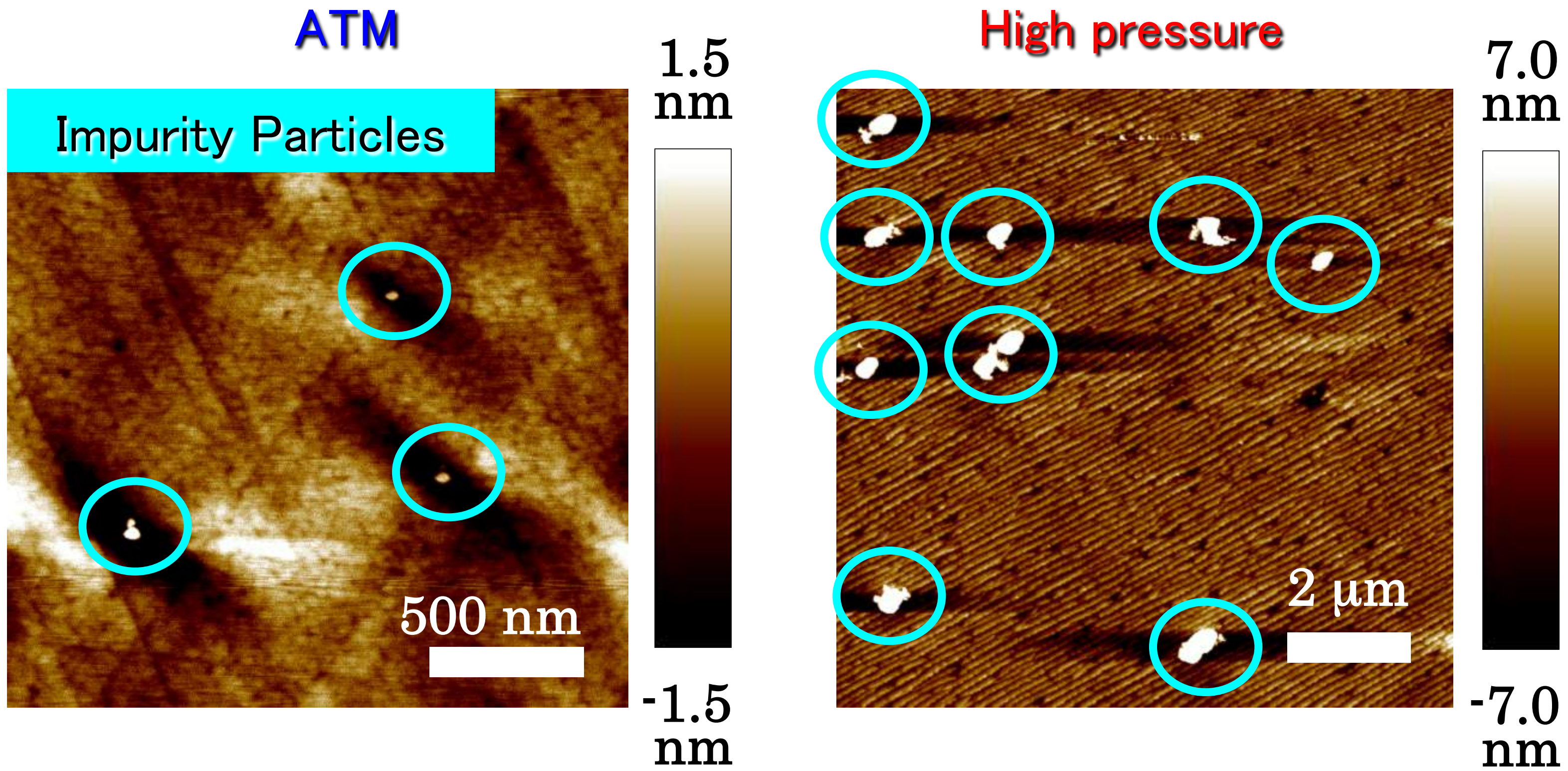




<u>The step terrace structure after the HP annealing</u> indicates clean and smooth surface

→ High pressure suppressed evaporation of Cu

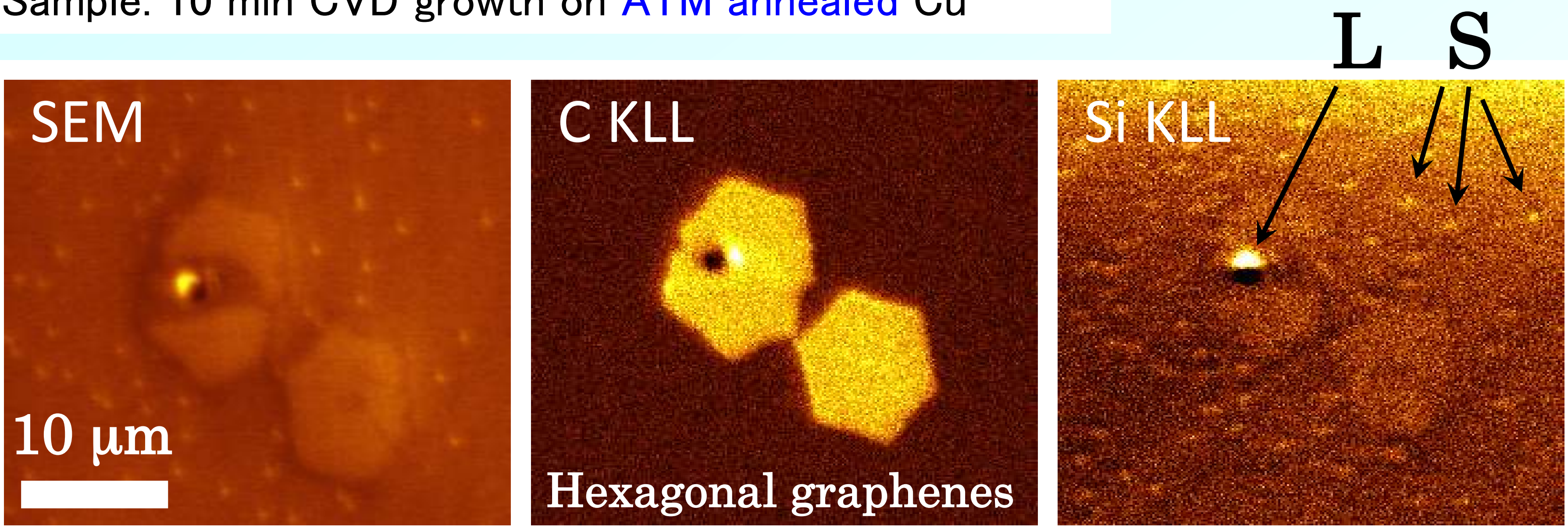
Impurity Particles on Cu



Sample	Density of particles ($1/\mu m^2$)	Height (nm)	Surface Structure	Density of graphene ($1/\mu m^2$)
ATM	0.86	5.2±0.6	-	7.5×10^2
HP	0.10	53±5	Step terrace	2.5×10^2

Auger Mapping of the Impurity Particles

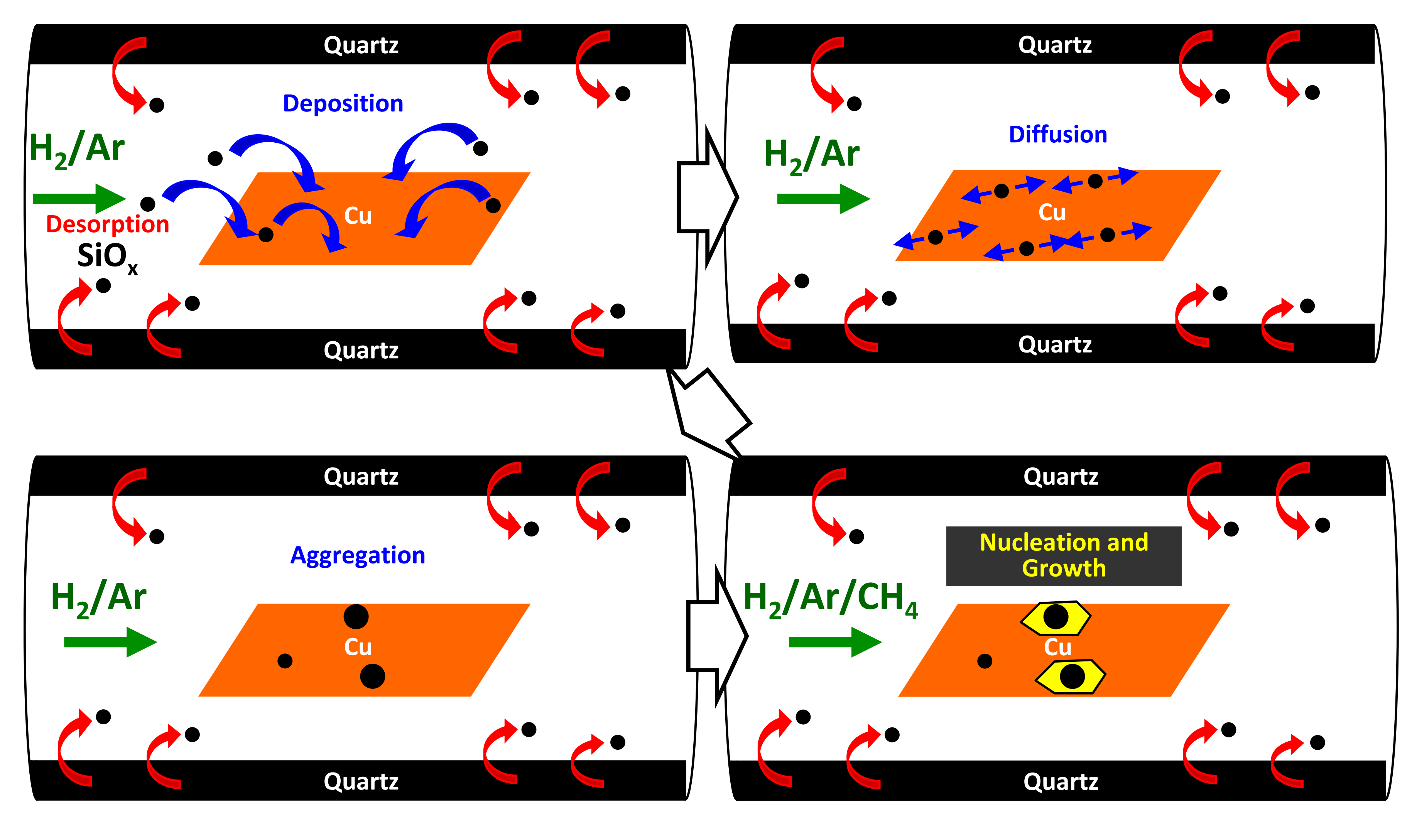
Sample: 10 min CVD growth on ATM annealed Cu



- The particle contains Si
- Large (L) particle was located on the center of graphene
- Many small (S) particles were on Cu substrate

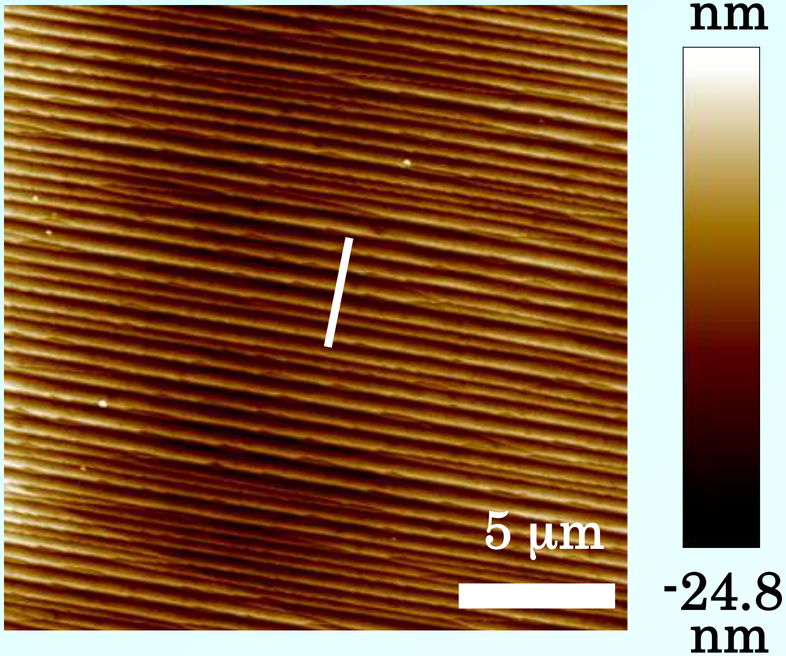
The impurity particles would be from the quartz tube

Particle-Assisted Nucleation



Electropolishing of Cu before annealing

Electropolishing + HP



Terrace width: ～400 nm
Density of particles: ～0.01 μm^{-2}

Sub-millimeter sized graphene

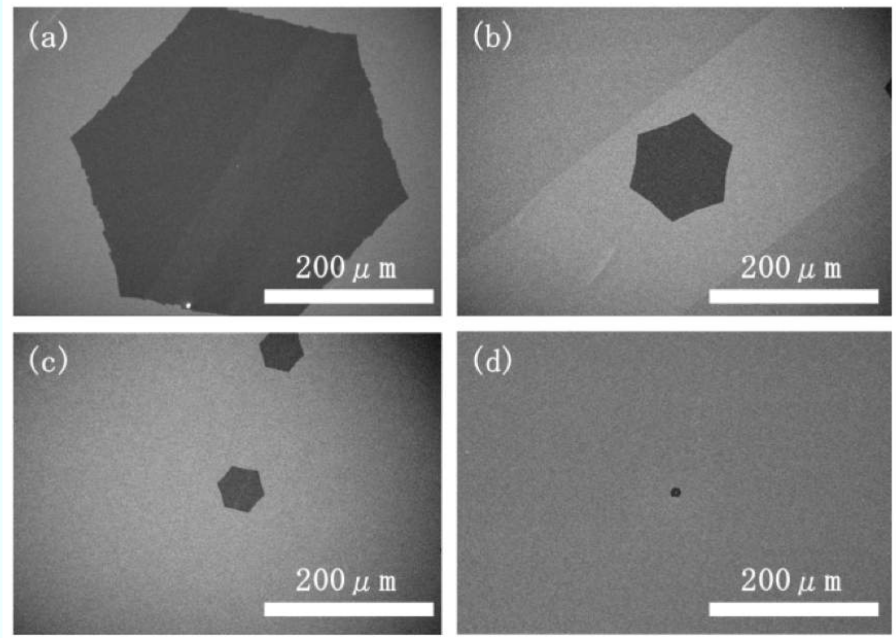


図 1．水素流量(a) 9，(b) 12，(c) 13，(d) 15 sccm，1050 ℃，45 分間の合成で得られたグラフェンの SEM 像.

- ◆ Electropolishing provided large terrace and low density of impurity
- ◆ Sub-millimeter graphene was grown through electropolishing and HP

Conclusion

- Effect of high pressure annealing of Cu on atmospheric CVD graphene growth was studied
- Role of high pressure annealing is suppression of evaporation of Cu → step terrace surface formation
- Auger imaging revealed that the Si containing particle was located on the center of graphene
- Particle-assisted nucleation process is suggested
- Combining electropolishing and high pressure annealing, submillimeter sized graphene growth was succeeded

Thank you for listening