Center for
Low-temperature Plasma Sciences

Evolution of Plasma Nanoprocess

Masaru Hori

Center for Low-temperature Plasma Sciences (cLPS), Nagoya University, *Japan*

https://www.plasma.nagoya-u.ac.jp/

Outline

- **Introduction**
  ~ *Self-organization* and *Self-limit reactions* ~

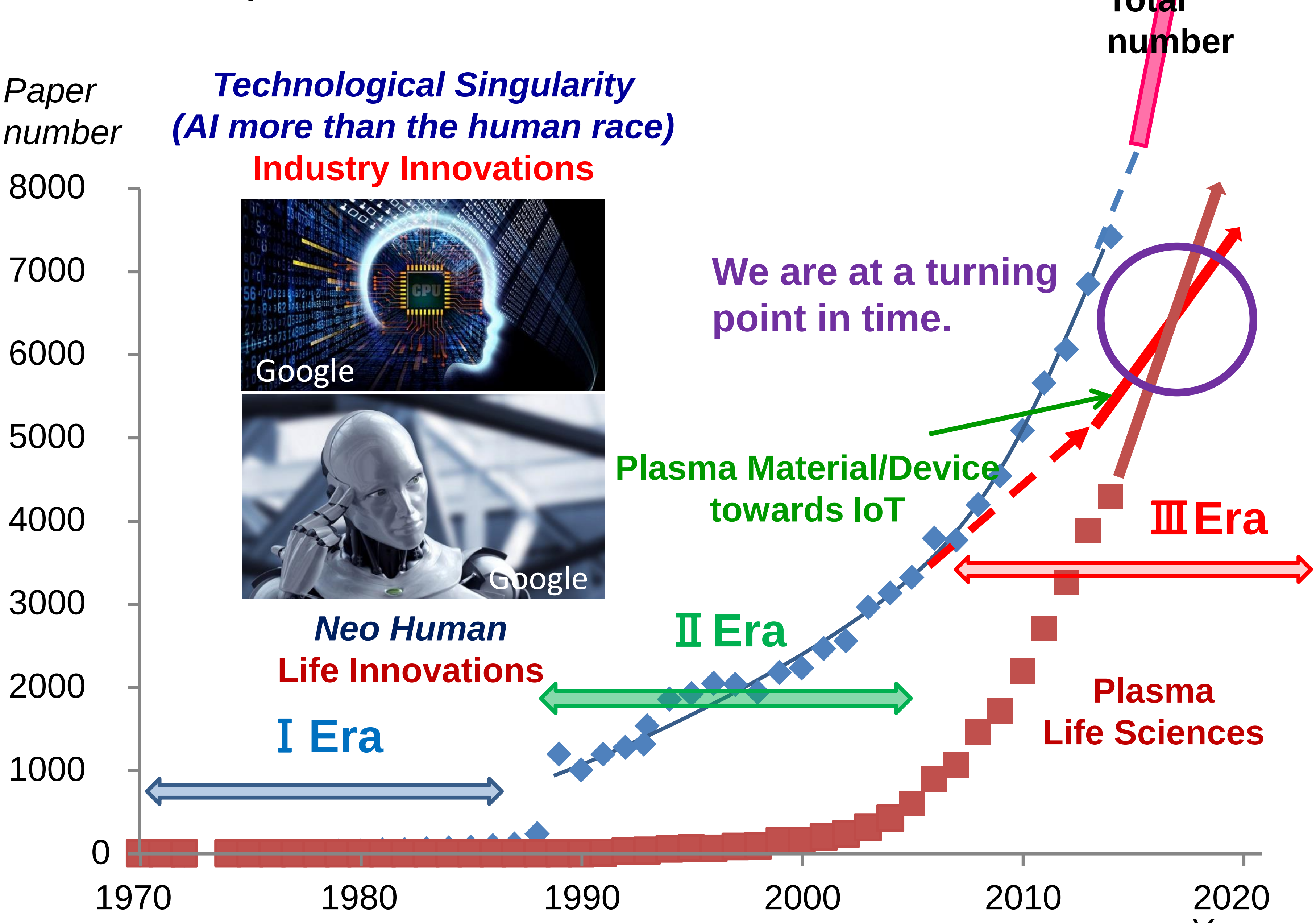
- **A challenge of fabrication of two dimensional nano-structure by a novel plasma etching with a *self-limit reaction***

- **Three dimensional nano-graphene (Carbon Nanowalls) formation by plasma induced *self-organization***

- **The Importance of real-time observation of plasma-induced surface reactions - Obtaining highly reliable basic science data**

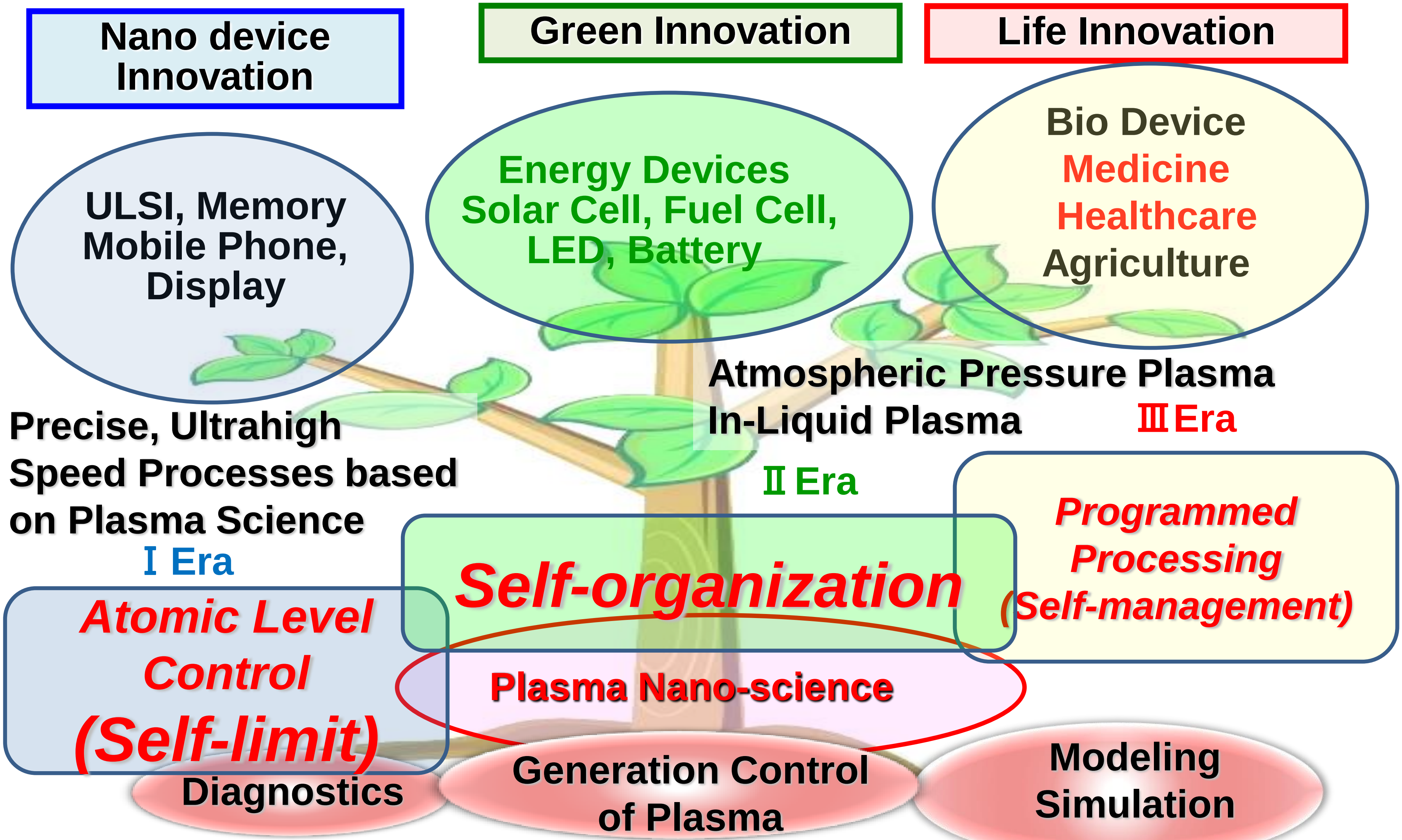
- **Conclusion**

Trend of Paper Number in Plasma Processes



Thomson Reuter Database

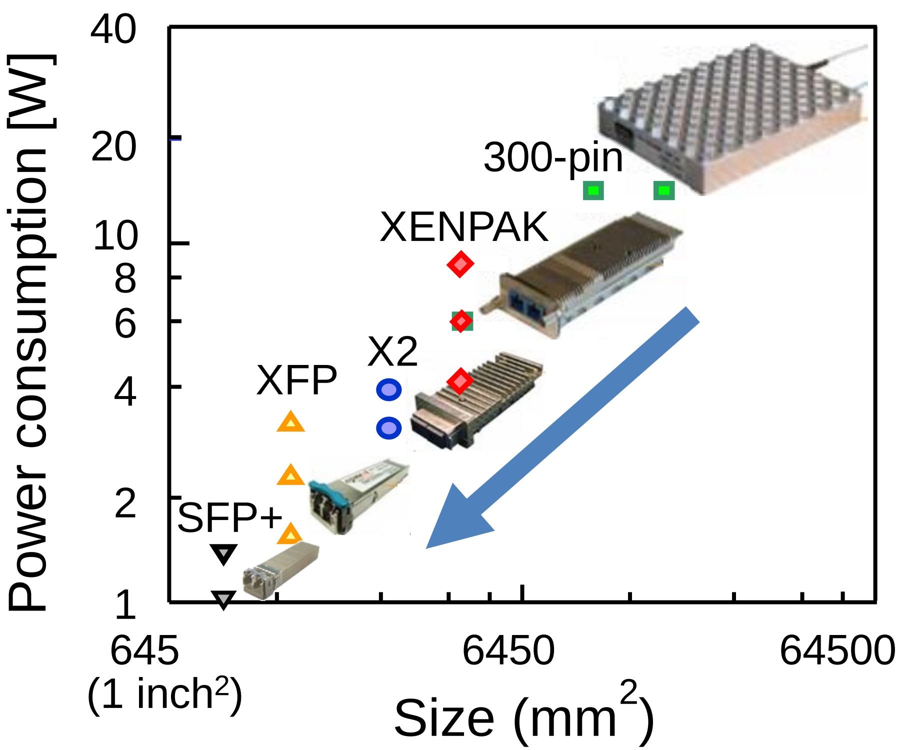
Plasma Nanoprocesses for Future Innovations

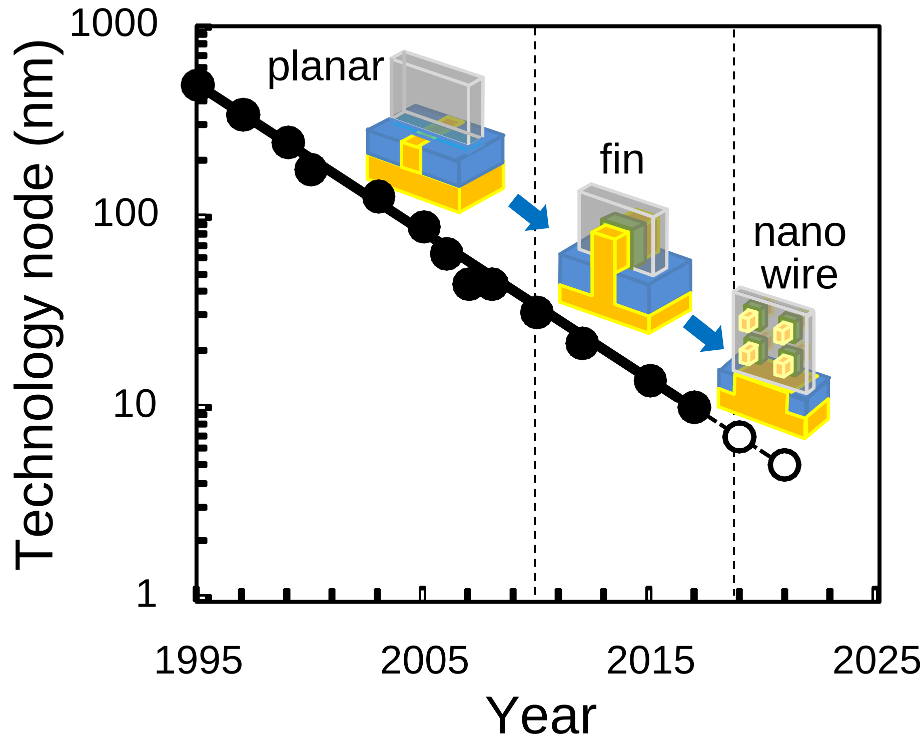


"*Plasma Informatics*" with AI should be driven by obtaining *reliable scientific data set (big data)* for plasma nano-science.

Technology trends

- Smaller transceiver require semiconductor laser that consume less power
- Technology node scaled down to <10 nm, atomic-layer process is required

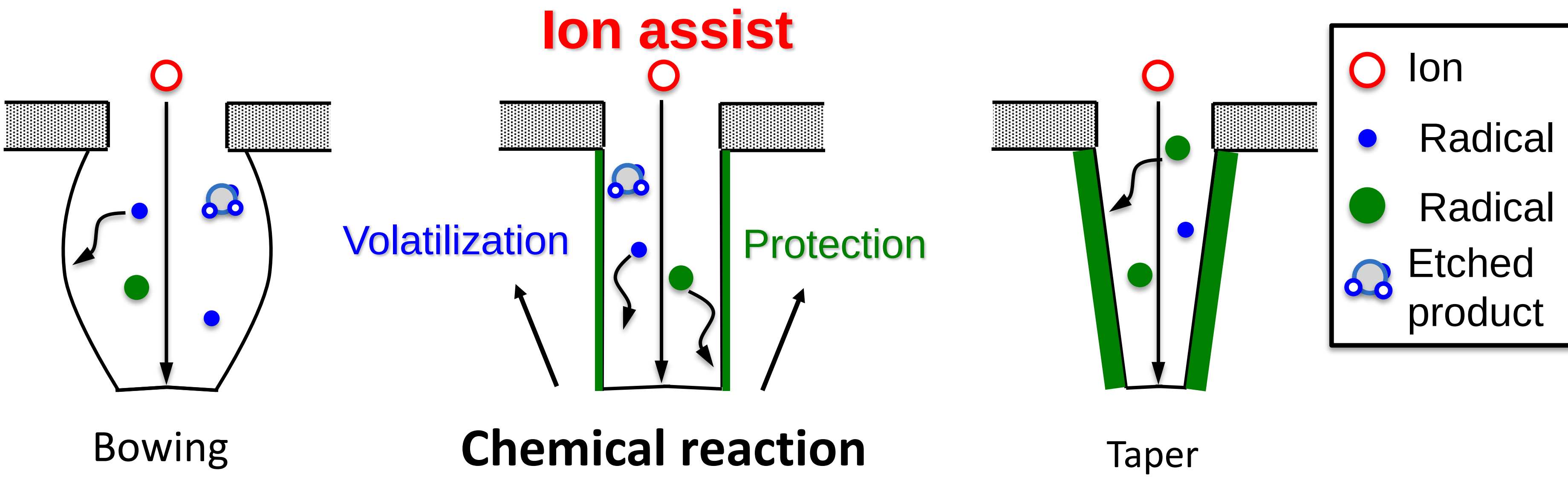




XENPAK: 10-Gb/s Ethernet transceiver package
XFP: 10-Gb/s small form-factor pluggable
SFP+: small form-factor pluggable plus

K. Shinoda *et al*., J. Phys. D **50**, 194001 (2017)

Important factors for etching (pattern size control)



Radical density, flux (ratio), Ion energy, Ion flux, Temperature, etc…

Chemical reaction -> Arrhenius equation

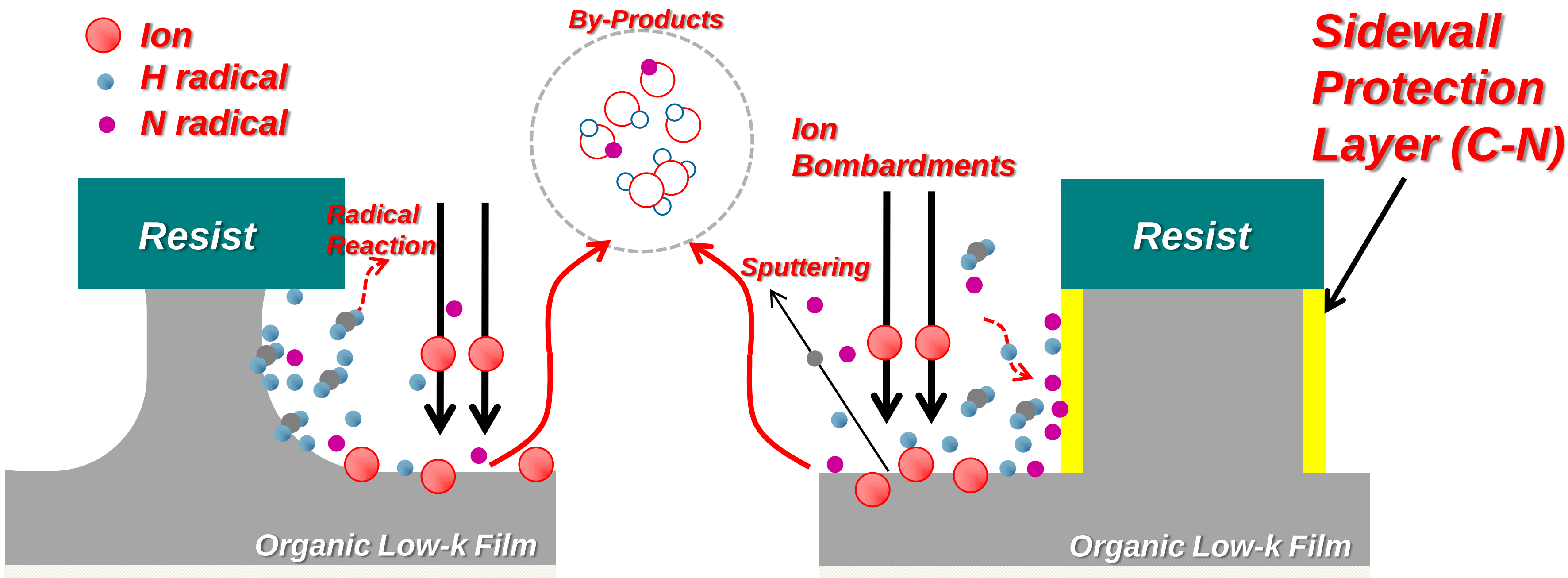
$$k = Ae^{-E_a / RT}$$

T : Absolute temperature
k : Rate constant
E_a : Activation energy
R : Gas constant
A : Frequency factor

Temperature	Low	High
Sticking	High	Low

Control of Radical density and substrate temperature has a key role in etching.

Model of Etching of Organic Film in H_2/N_2 Plasma



(1) Etching species, such as the atomic H radicals and NH_x^+ ions, enhance the etching rate.

(2) Modification of the surface to form a nitride amorphous carbon (a-CN) layer protects the organic film against spontaneous chemical etching.

(3) Etching products are desorbed in the form of C_xH_y and HCN molecules and composition of the products is strongly dependent on the incident ionic species.

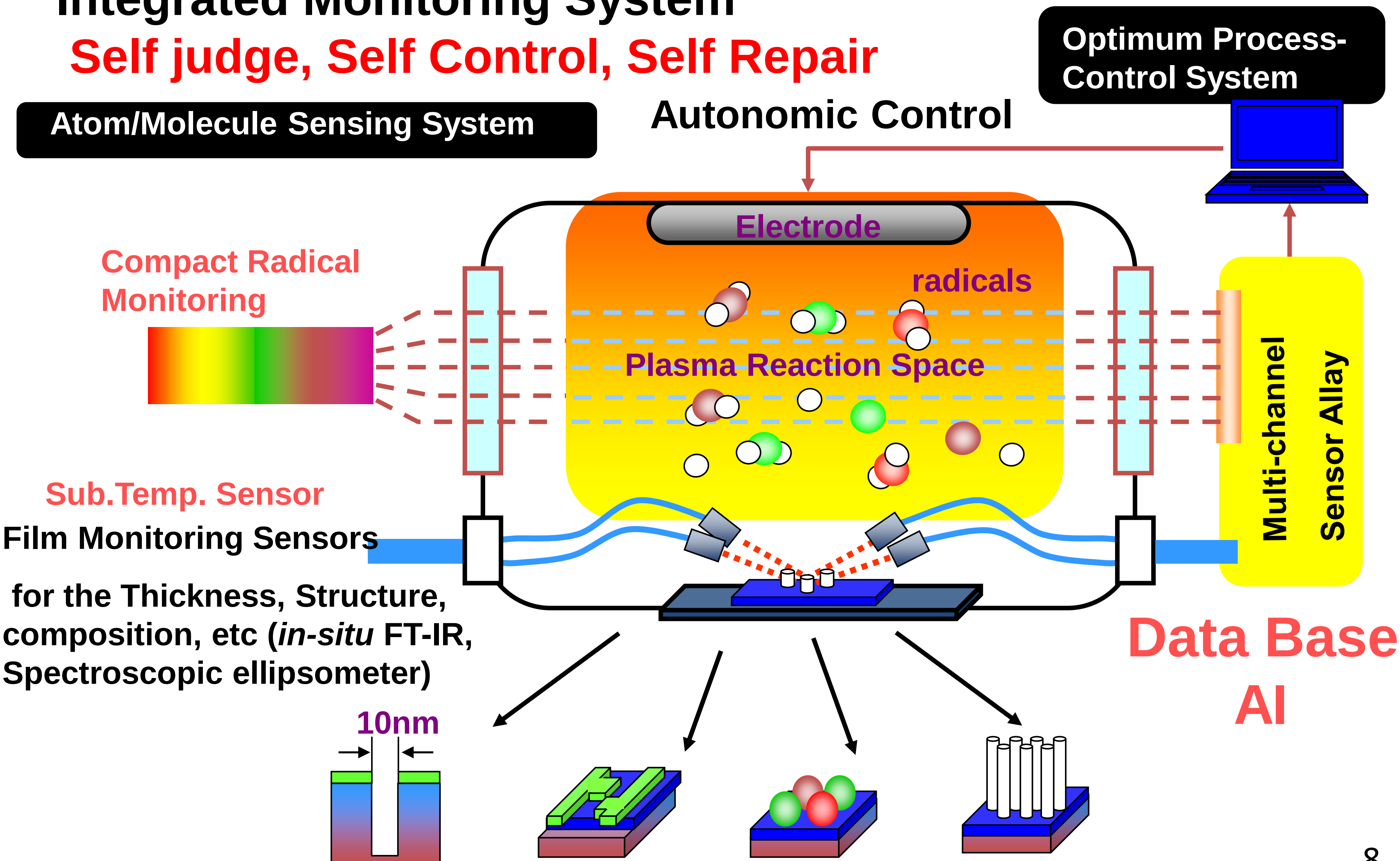
Side wall protection layer (thickness) is extremely important for nano-size pattern.

Autonomic Controlled Nano-Production System

（Proposal: 2002, Invention: 2006, demonstration of effectiveness: 2008)

Integrated Monitoring System

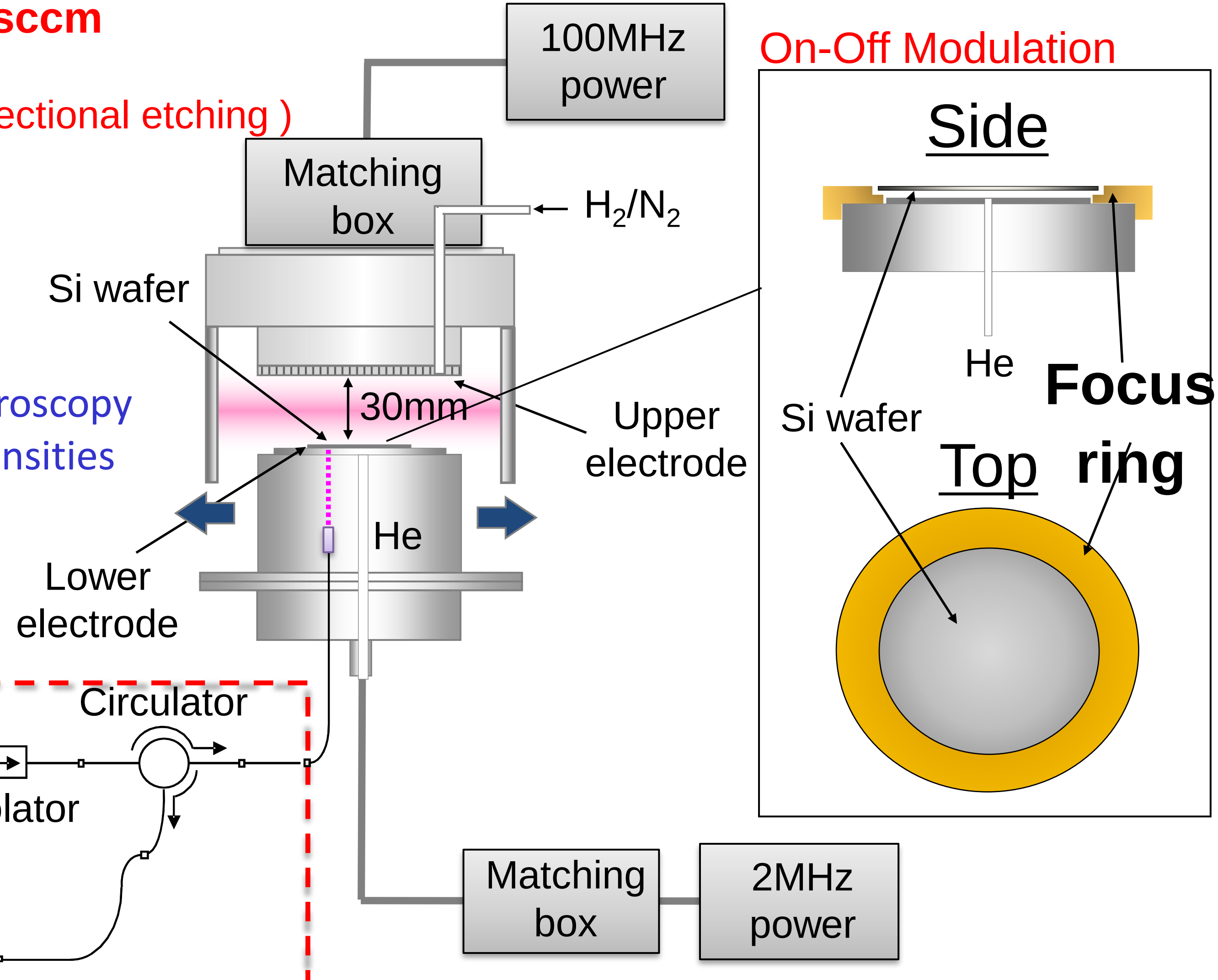
Self judge, Self Control, Self Repair

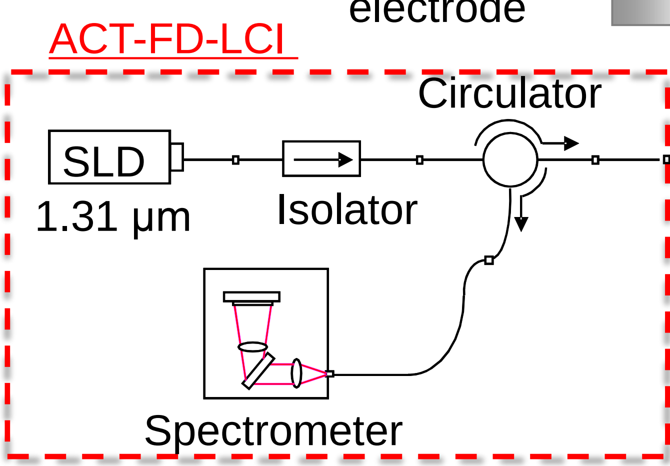


Experimental setup for etching of organic films

Gas : H_2 / N_2 = 75 / 25 sccm
100 MHz power : 400 W
2 MHz power : 200 W (Directional etching)
0 W (Trimming)
Pressure : 2 Pa
Coolant temperature :
10, 50, 90^{o}C

VUV absorption spectroscopy
For H and N radical densities

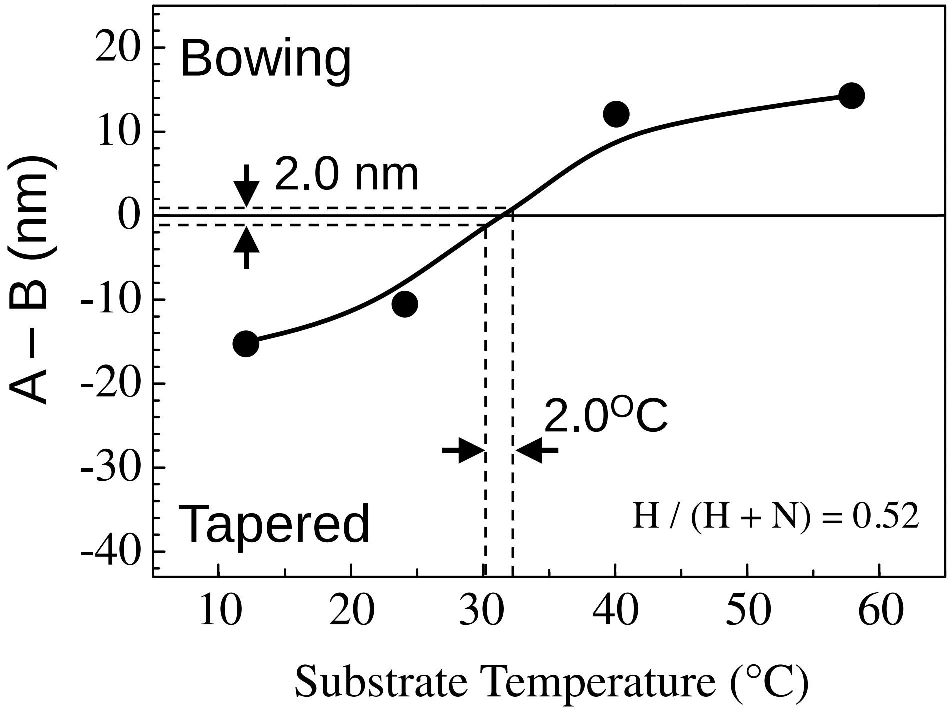


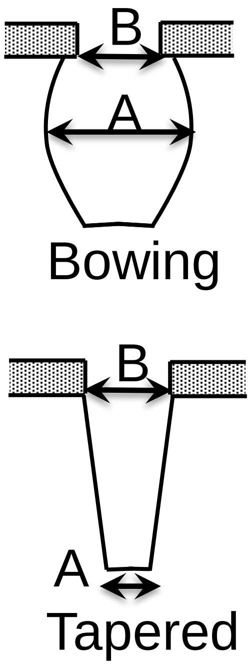


Frequency-Domain Low-Coherence Interferometry (FD-LCI)

Wafer temperature and etched profile of organic film

H / (H+N) = 0.52, which was monitored and controlled.



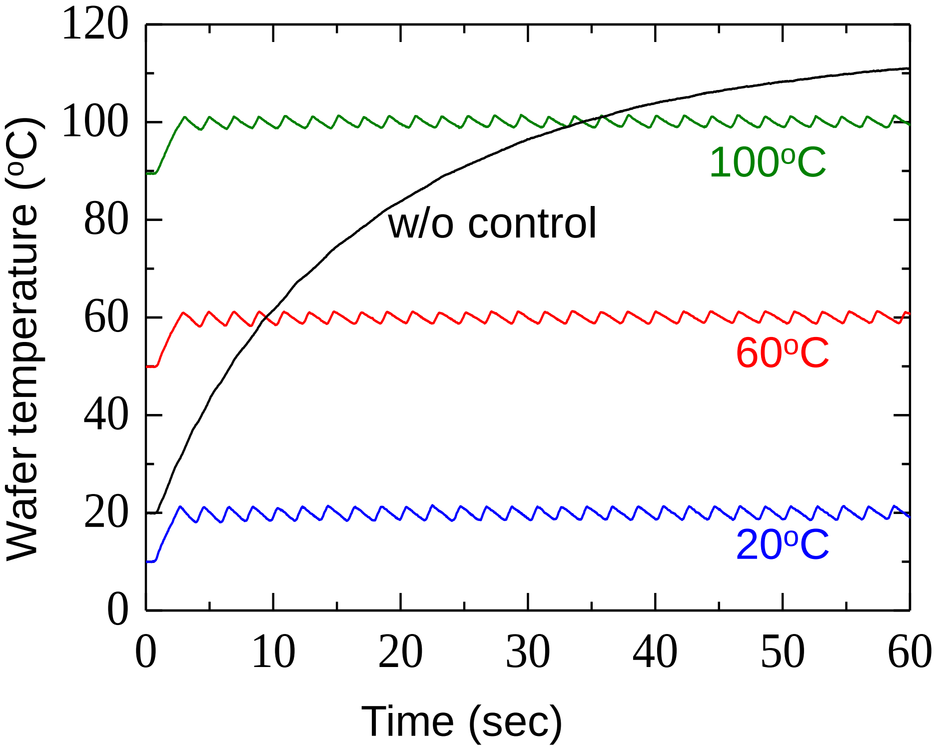


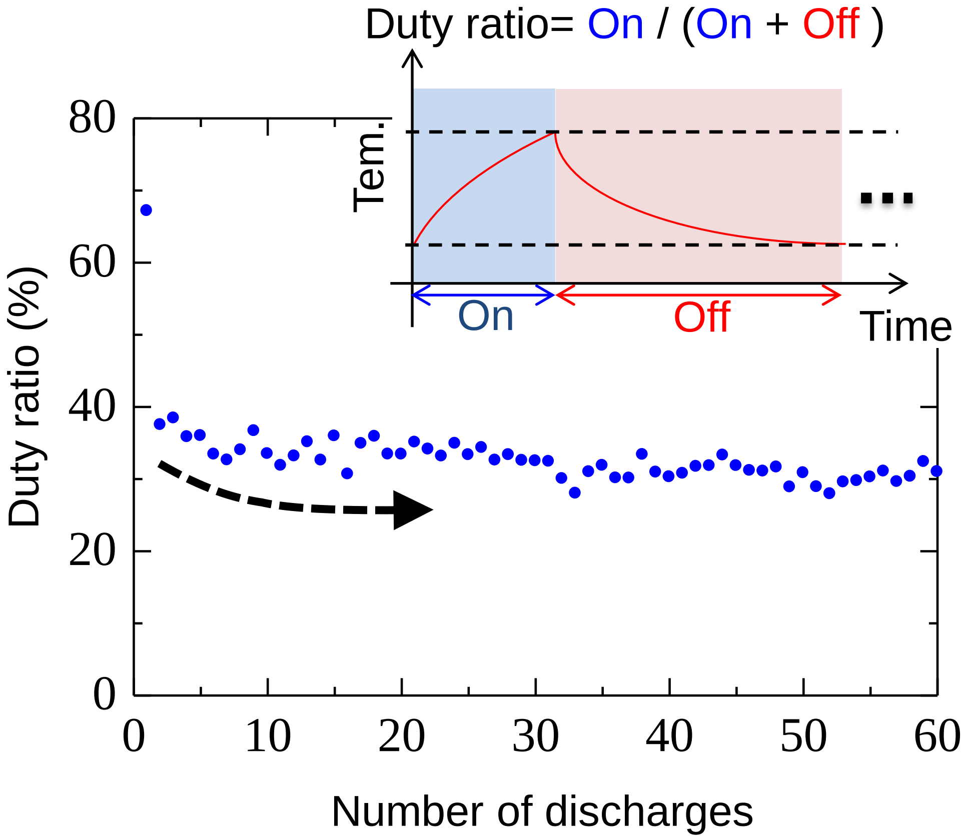
Substrate temperature should be controlled within several degrees to achieve nm-scale precision (1nm size fluctuation caused by 1 °C).

Develop a wafer-temperature control system
to realize etch process with a nm-scale precision

H. Yamamoto *et. al.*, J. Appl. Phys. **51** (2012) 016202.

Temporal variation of the wafer temperature during etching



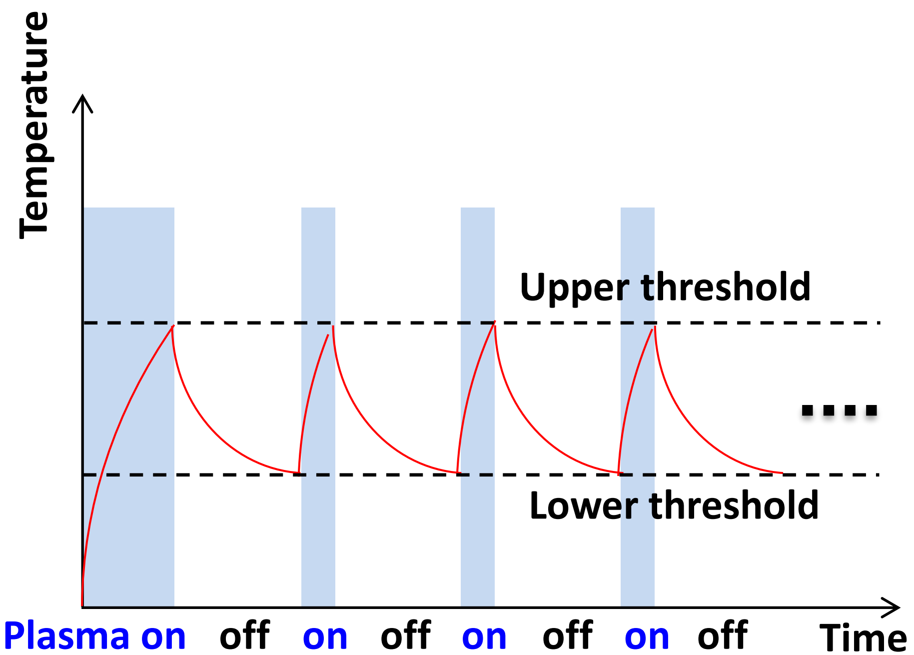


・Usually difficult to maintain the temperature in conventional pulse discharges

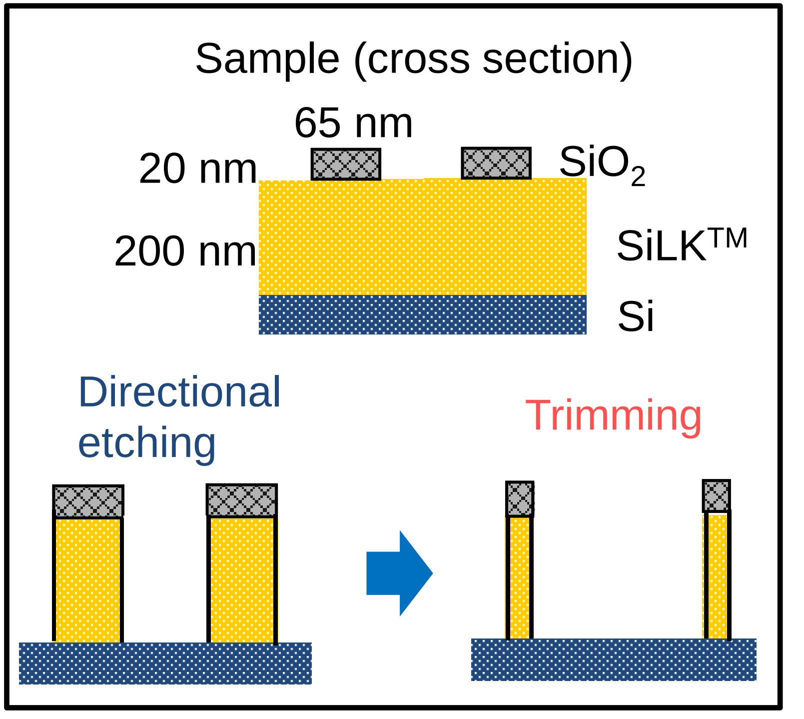
・The system makes the wafer temp. keeping within a few Kelvin by autonomously controlled pulse plasma according to monitoring of temperature

Temperature control (On-Off Modulation of Source Power)

1. Feedback control of wafer temperature using Frequency-Domain Low-Coherence Interferometry (FD-LCI)
2. Directional etching and trimming processes of organic films with the feedback control system.



1. Feedback Control of Wafer Temp.

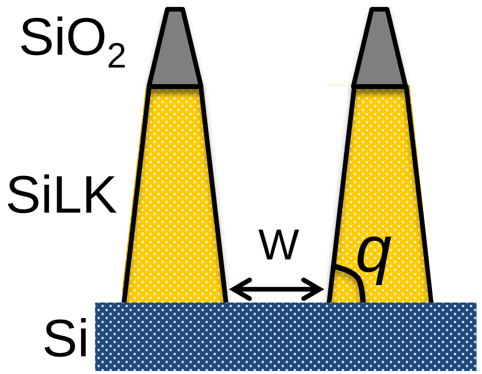


2. Evaluating temp. dependence of etched properties

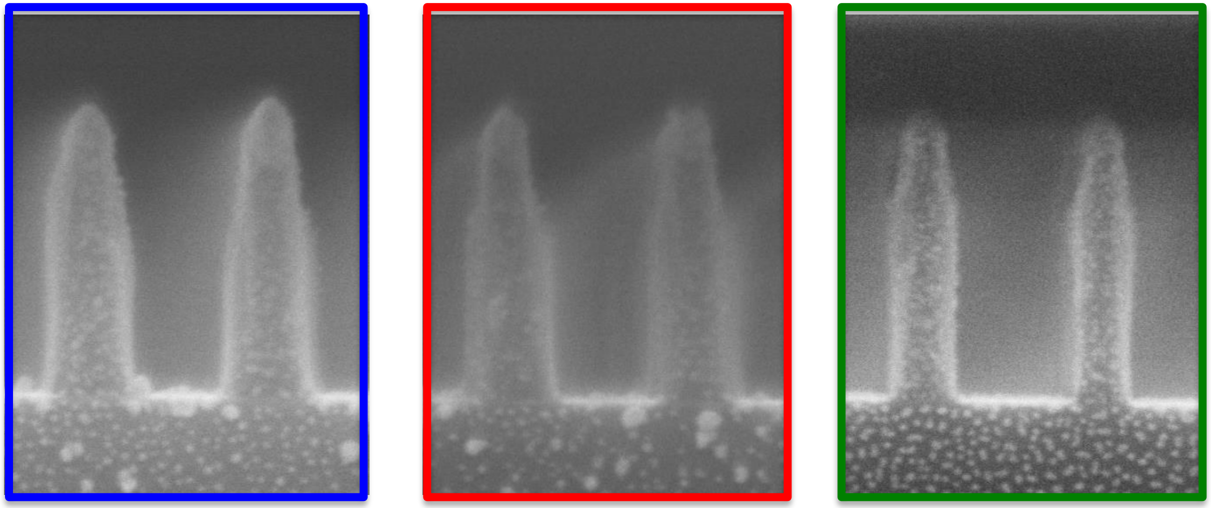
T.Tsutsumi, Y. Fukunaga, K. Ishikawa, K. Takeda, H. Kondo, T. Ohta, M. Ito, M. Sekine, M. Hori
Feedback Control System of Wafer Temperature for Advanced Plasma Processing and its Application to Organic Film Etching
IEEE Trans. Semicond. Manuf. 28 (4) (August, 2016) pp. 515-520, DOI: 10.1109/TSM.2015.2470554

Etched feature of organic film depending on temperature

H / (H+N) = 0.52



Etched profiles at 50 s



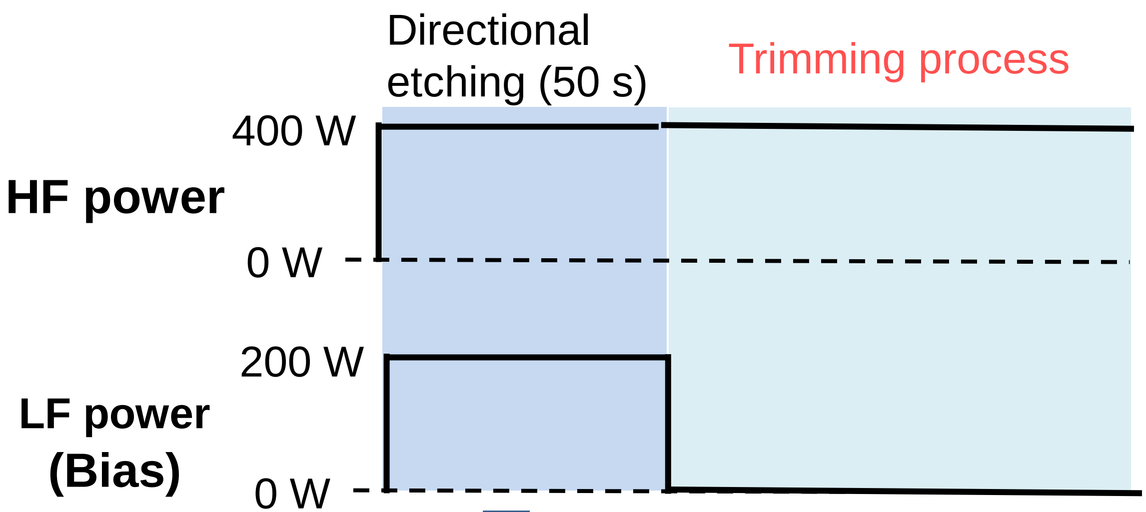
20°C 60°C 100°C

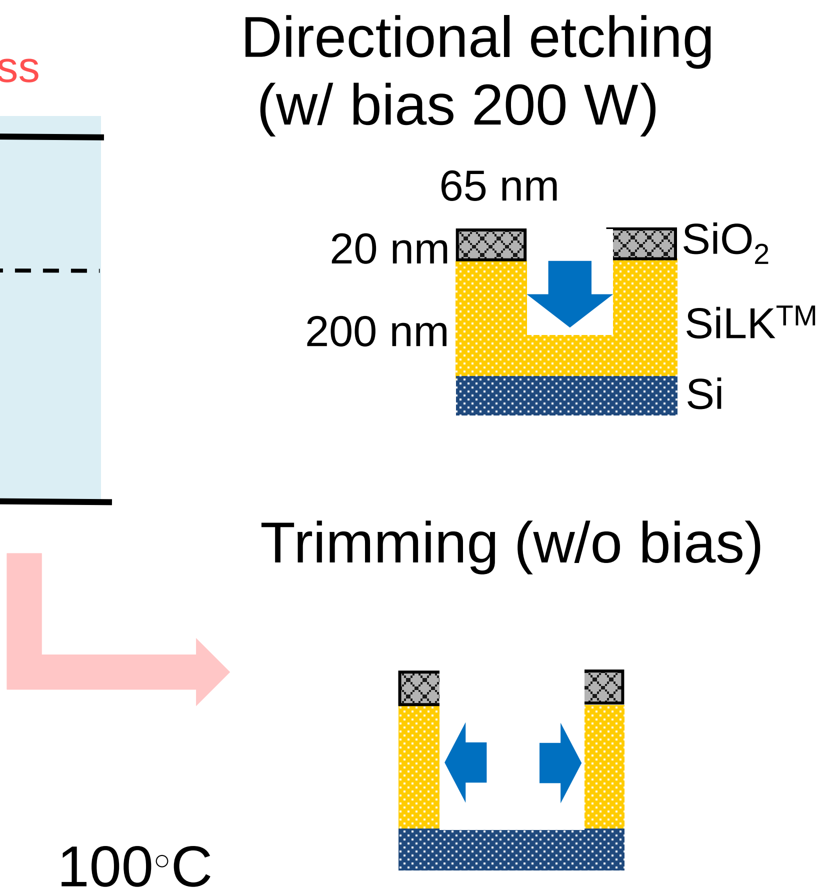
Slope θ : 81.5 → 84.3° → 87.3°

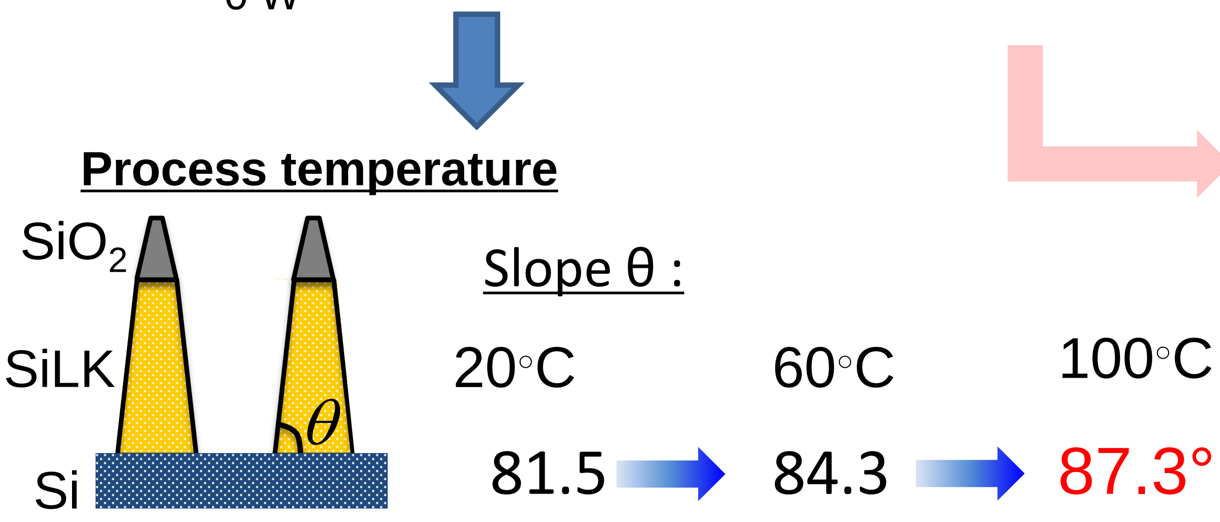
The etched profile control with high accuracy can be achieved by controlling the wafer temperature.
Etched profile became vertical with increasing temperature.

These results might be, for the first time, the real etching data with ***a constant substrate temperature!***

Process sequence of Trimming Process



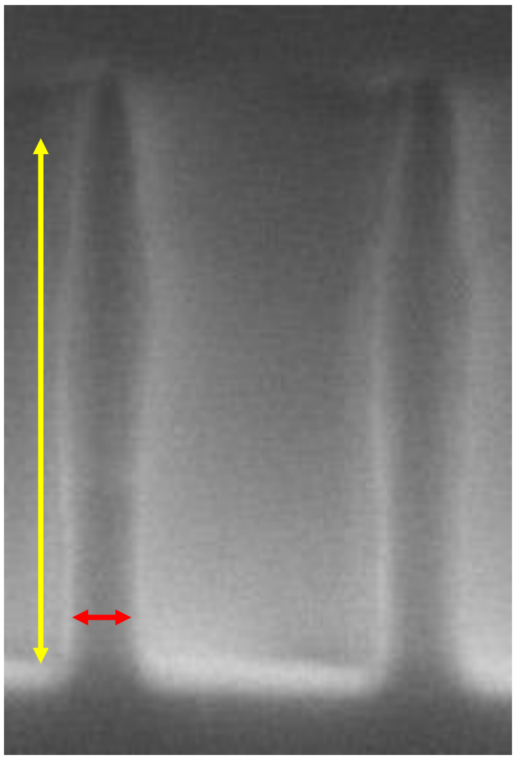




Trimming process was performed at a constant 100℃.

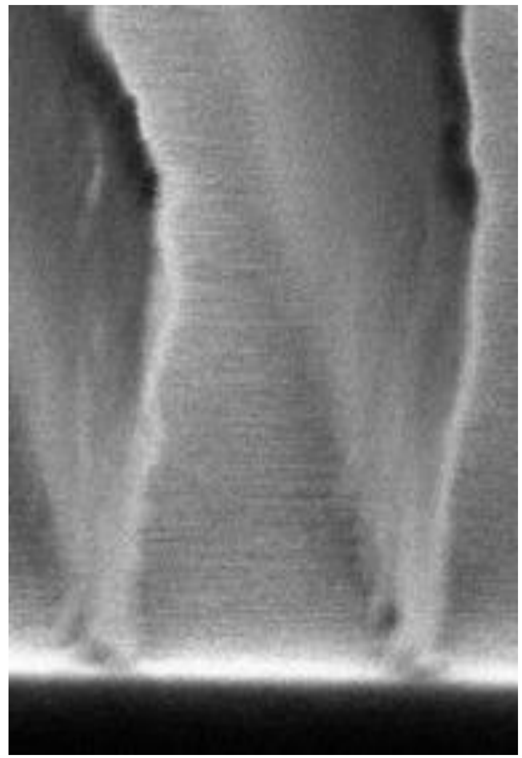
A new self-limited processing
(Possibility of no-fluctuation in size)

50 s



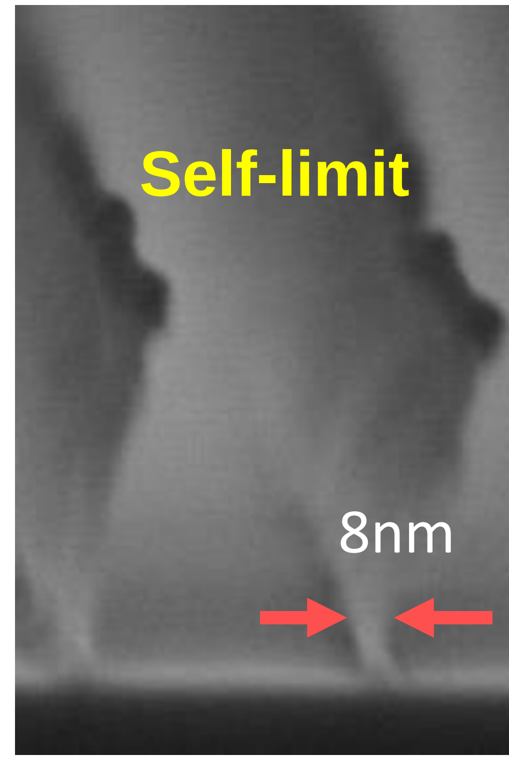
Height: 200 nm
Width : 35 nm

150 s



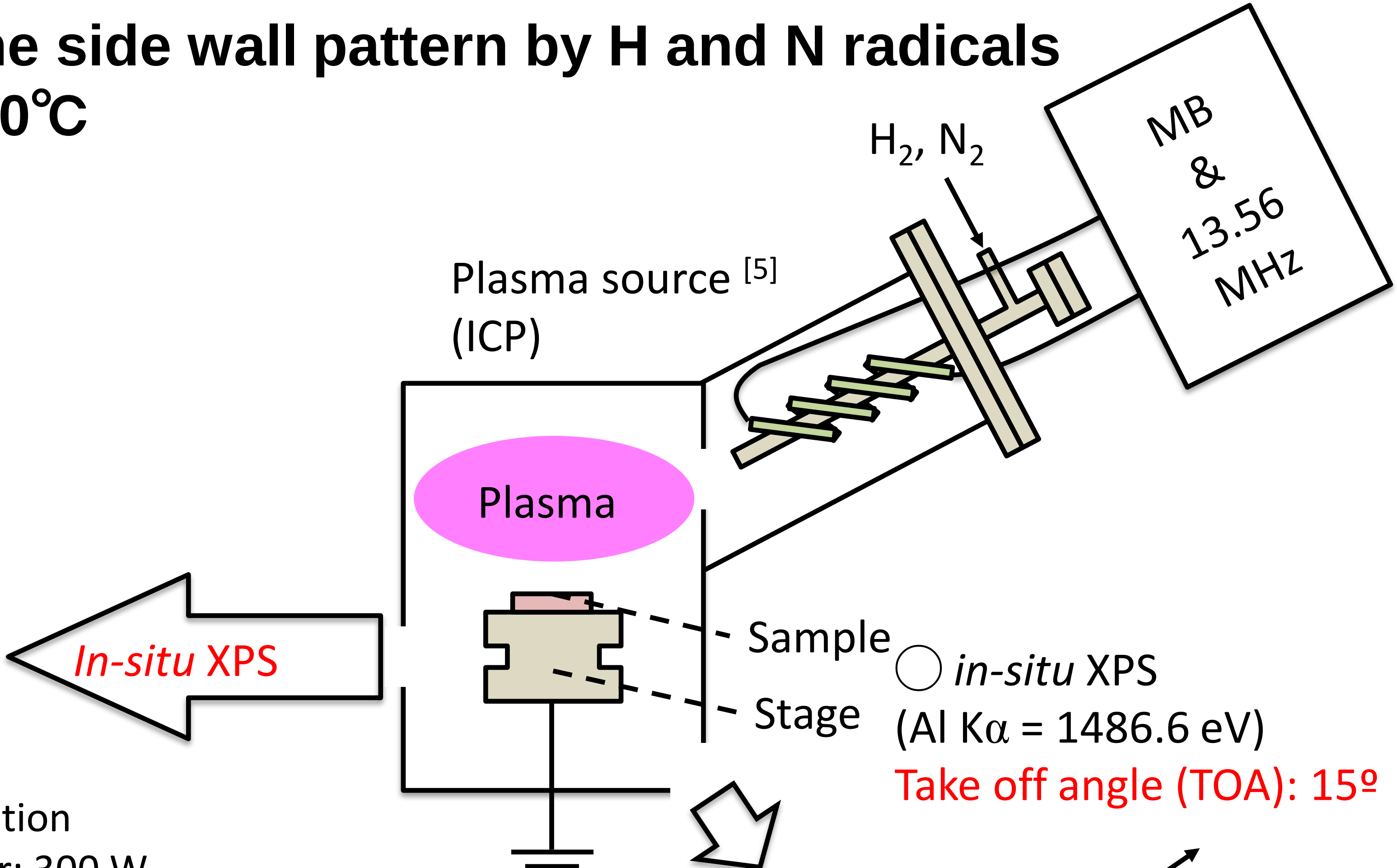
Height : 150 nm
Width : 10 ~ 15 nm

350 s

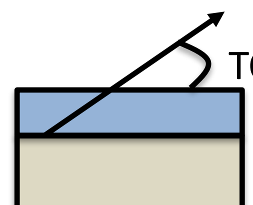


Height : 130 nm
Width : 8 ~ 13 nm

To simulate chemical reactions on the side wall pattern by H and N radicals at 100℃



○ *in-situ* XPS
(Al Kα = 1486.6 eV)
Take off angle (TOA): 15º

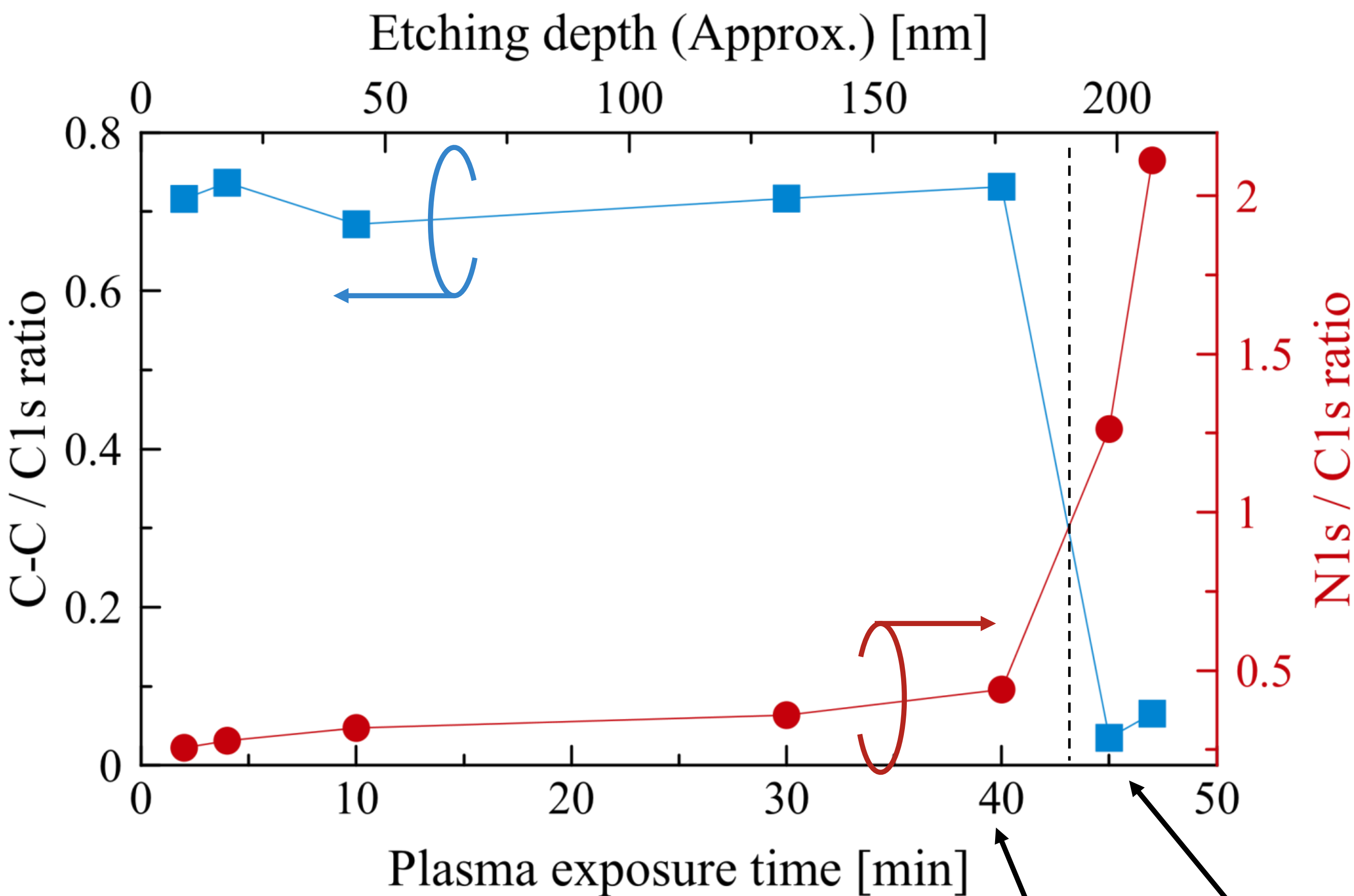


Condition
Power: 300 W
Gases: H_2 / N_2 = 15 / 5 sccm
Pressure: ~ 0.2 Pa
Temp. : ~100ºC

Analysis the organic surface treated by H_2/N_2 plasma by *in-situ* XPS

[6] S. Chen, *et al.*, Jpn. J. Appl. Phys. **50** (2011), 01AE03.

Carbon / Nitrogen ratio



Thickness (assumption):	~27 nm	**~5 nm** (Etching Stop)

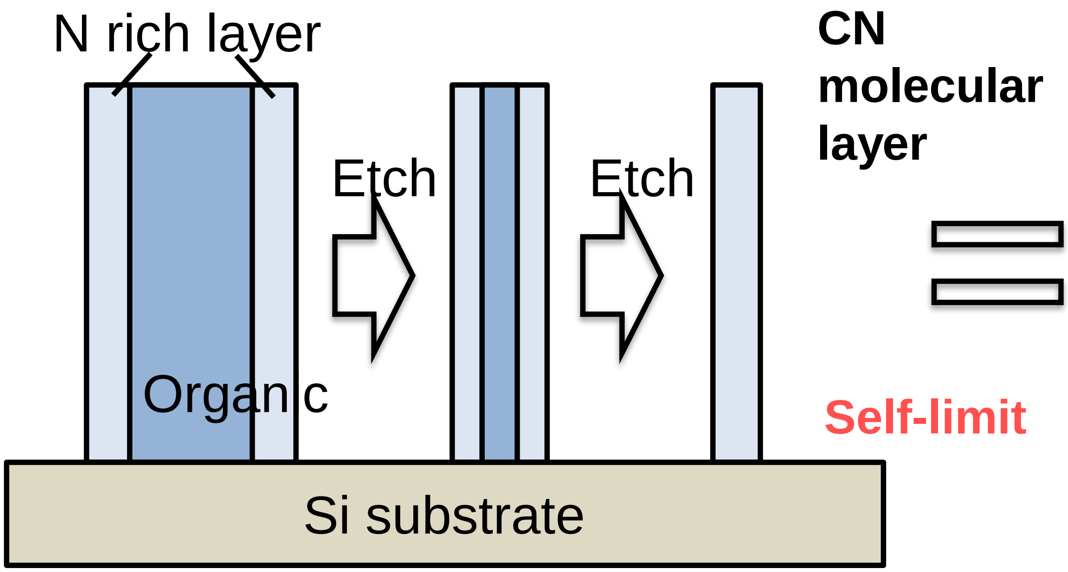
Self-limit

C-C bond : less than 10% (CN: more than 90%)

N rich (N/C ratio: more than 100%)

A new nano-patterning with a self-organization

Successfully formed high aspect structure of nanocarbon film with self-limited process by controlling temperature and radical ratio.



100ºC, 350 s

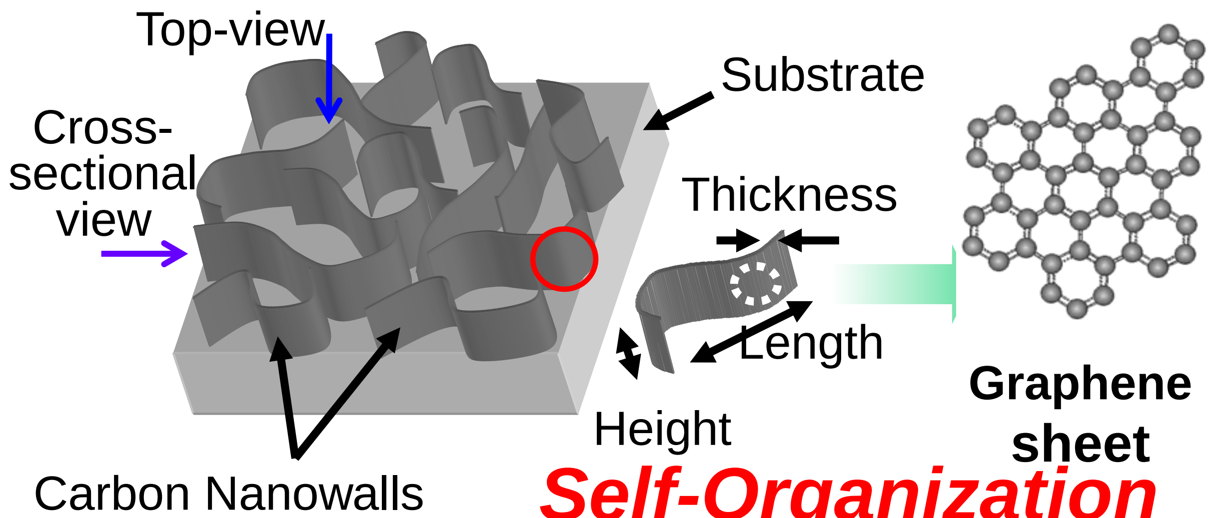
Height : 130 nm
Width : ~ 8 nm

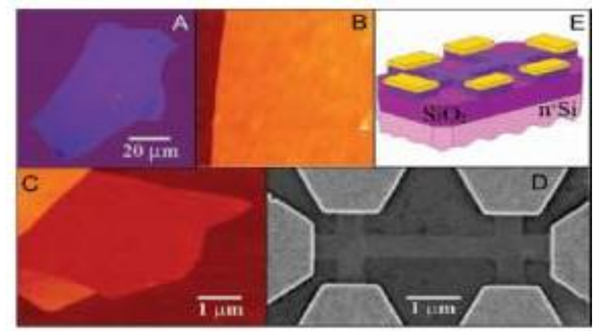
No-Fluctuation of Pattern size!
The molecule process with controlling radicals will be studied.

- CN layer film has excellent mechanical properties, optical properties
- Possibility as a novel method of 3D nanocarbon pattern.

Fukunaga Yusuke, Tsutsumi Takayoshi, Kondo Hiroki, Ishikawa Kenji, Sekine Makoto, Hori Masaru, JAPANESE JOURNAL OF APPLIED PHYSICS , 58, 2, 2019

Self-Organization :Three Dimensional Graphene (CNW) synthesized by plasma

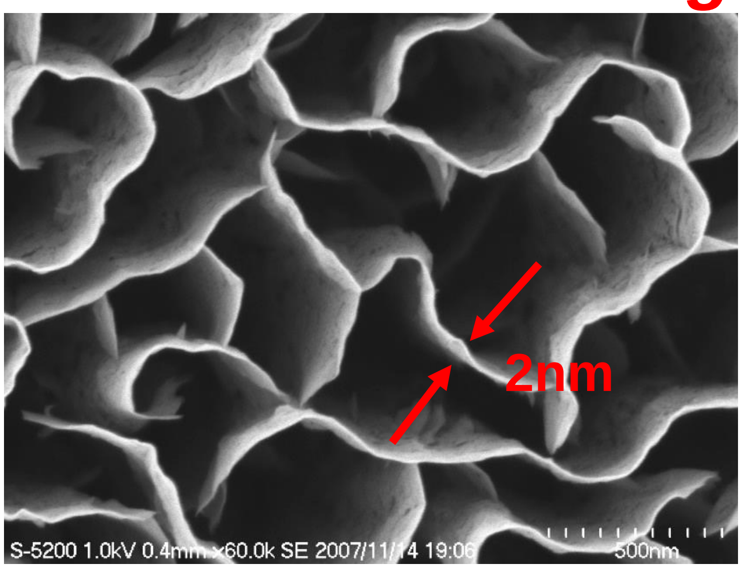


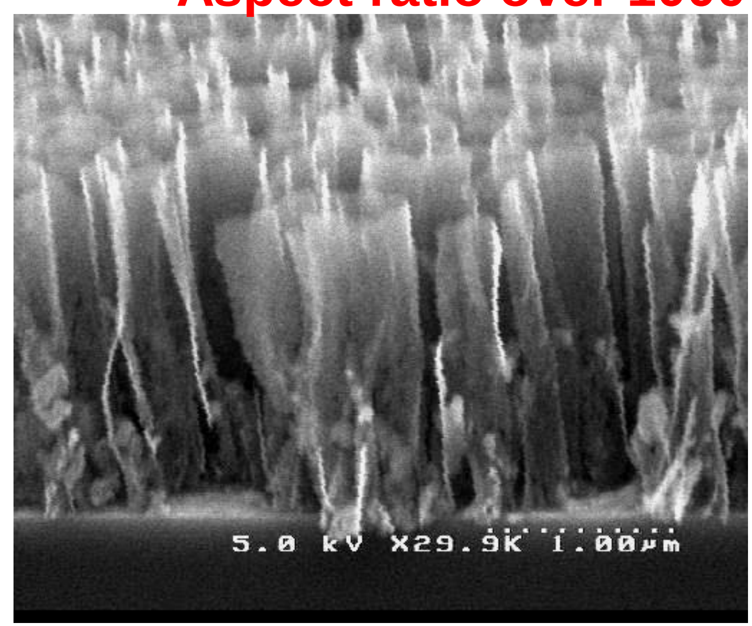


K. S. Novoselov, A. K. Geim, et al.: SCIENCE, Vol. **306**, 666 (2004).

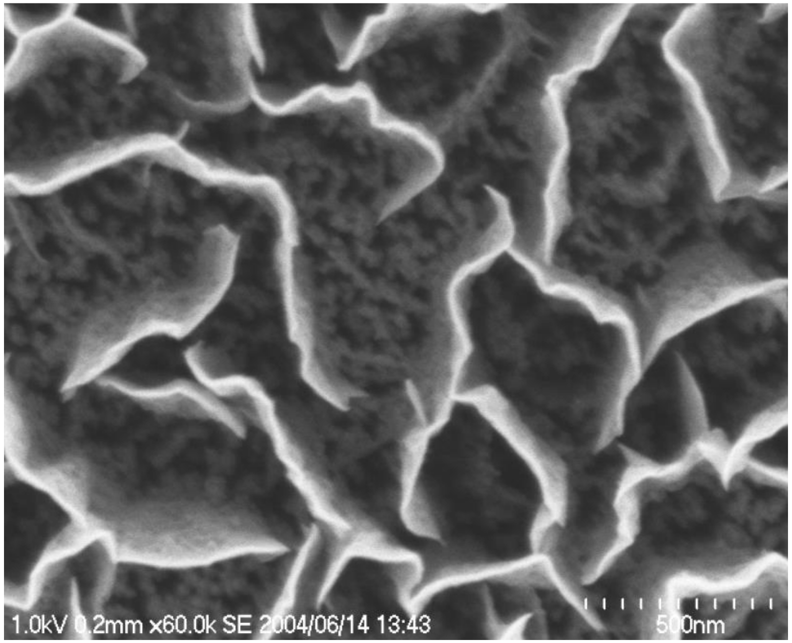
Self-Organization

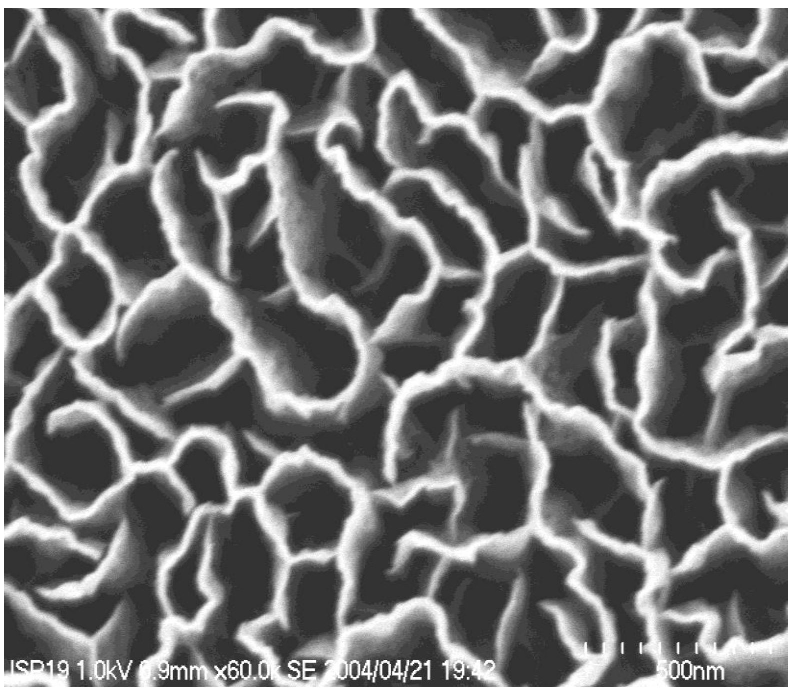
Aspect ratio over 1000





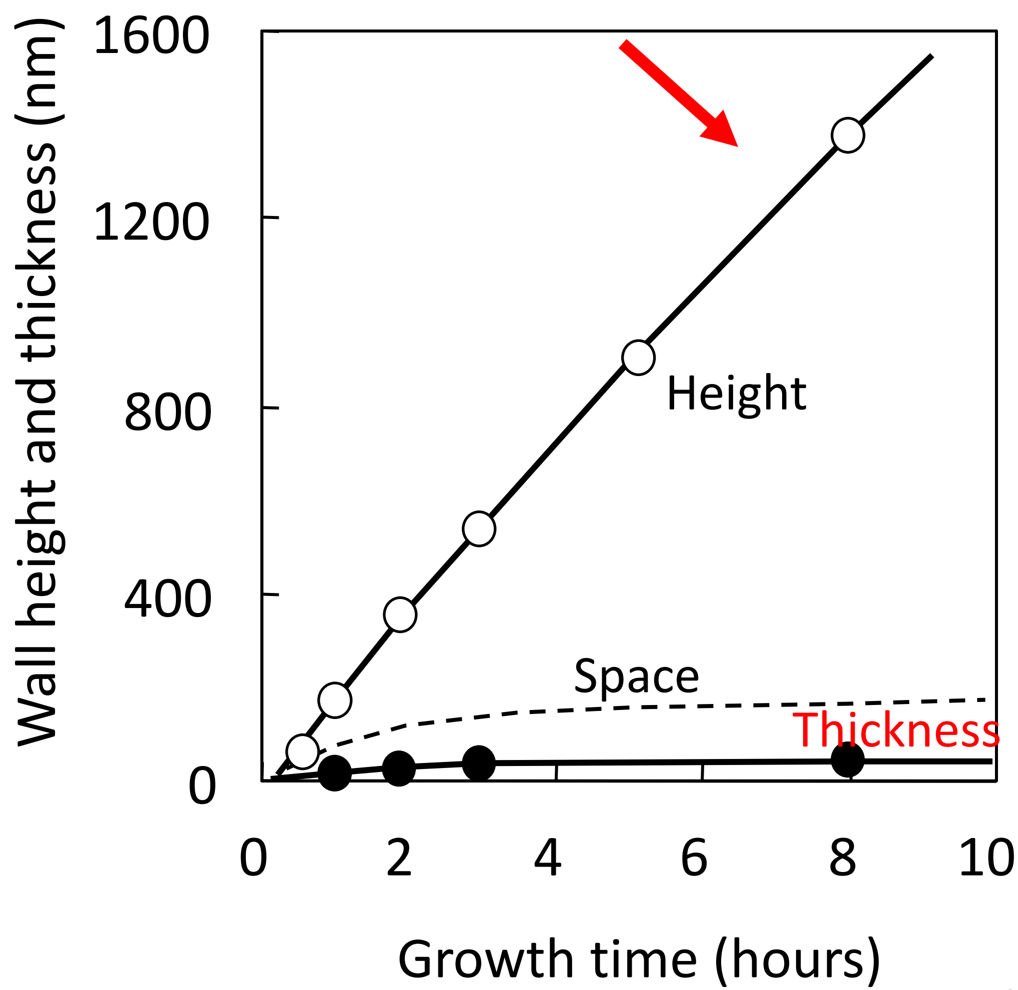
M. Hiramatsu and M. Hori : Appl. Phys. Lett., 84, 4708 (2004)
28 patent registrations, 62 patent applications.



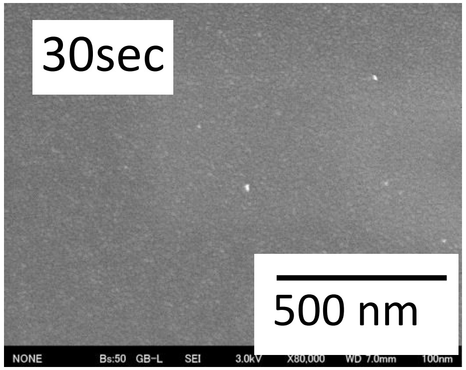


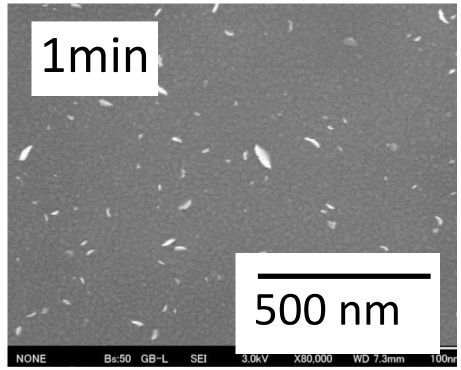
Self Organization Growth By Plasma Nanoprocessing!

Ultrahigh Aspect Ratio over 400



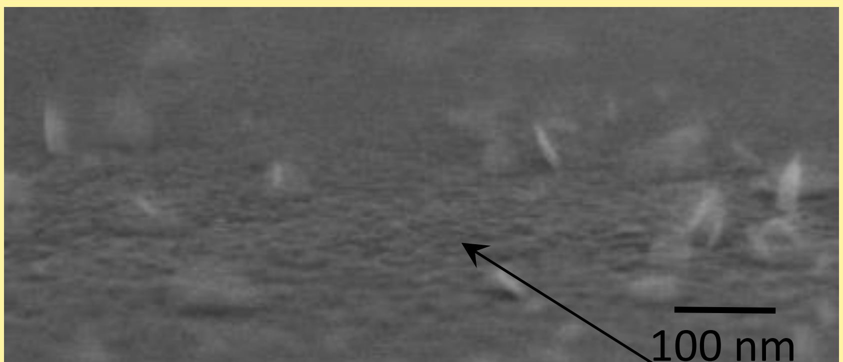
Observation of early stage of CNW growth



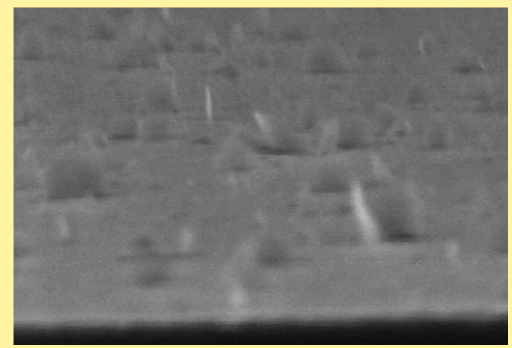


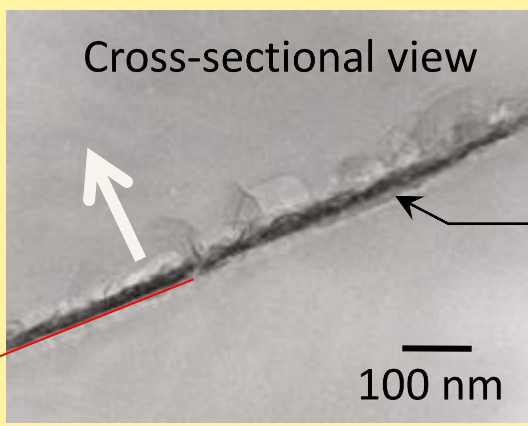
Coverage with amorphous carbon layer

Onset of isolated nanosheets

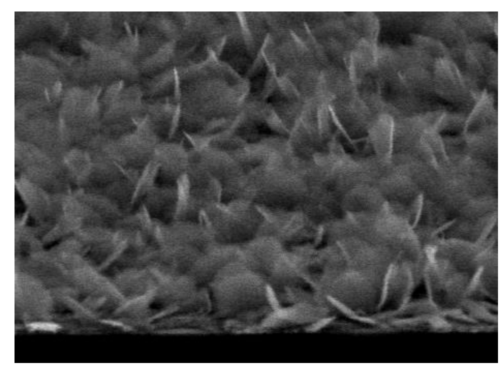


2 min





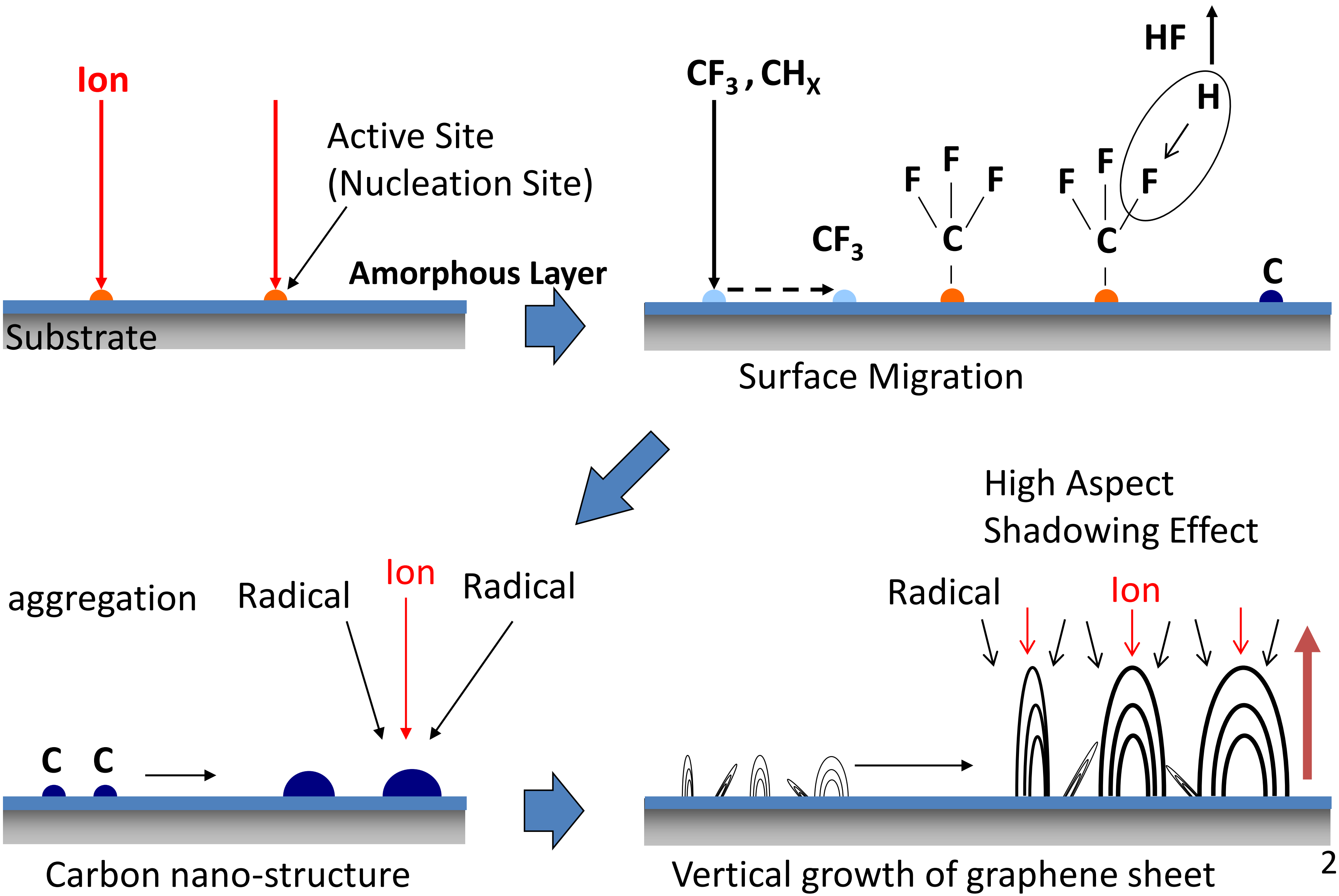
Amorphous carbon layer (10-30 nm)



5 min

Carbon Nanowall Growth Mechanism

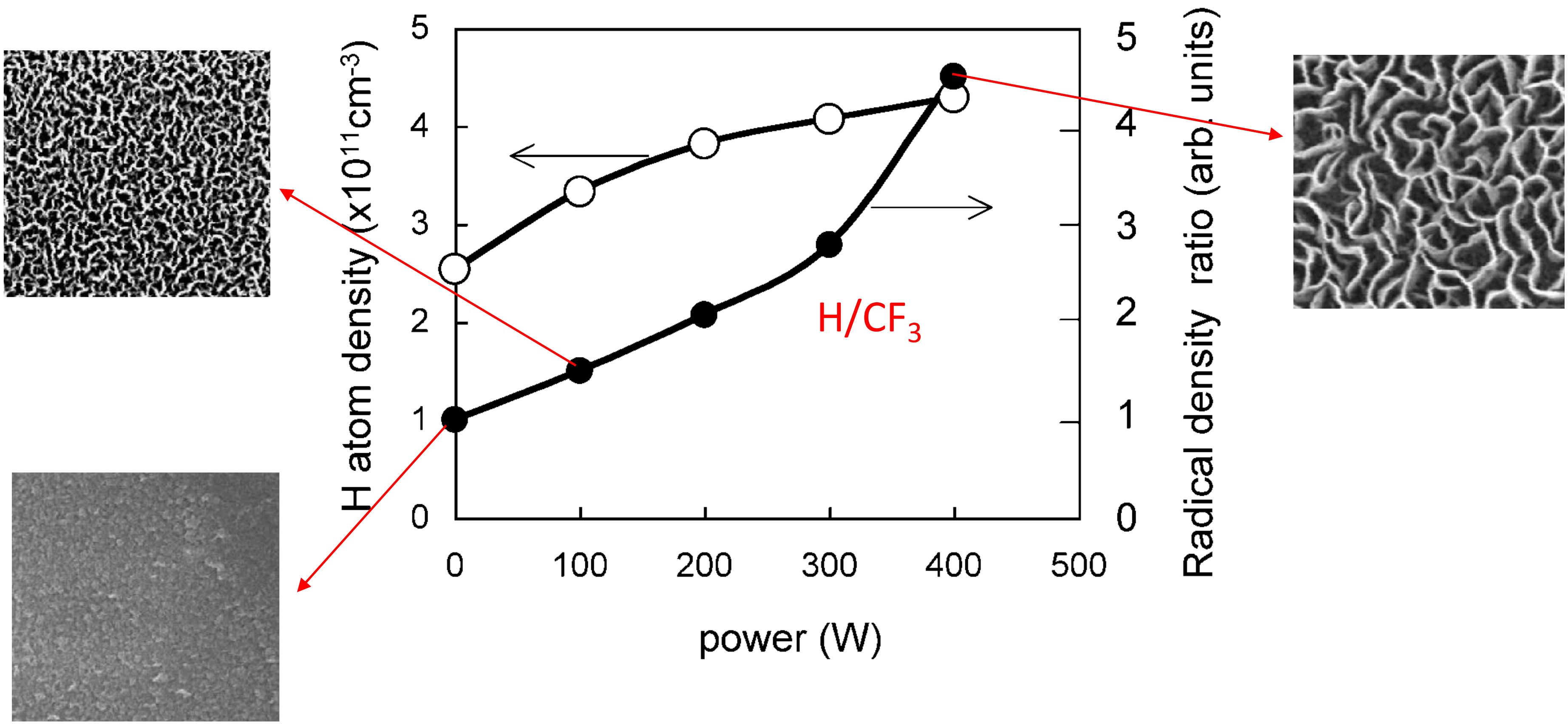
Plasma Induced Self-organization Process



Radical density ratio (H/CF_3) vs. morphology

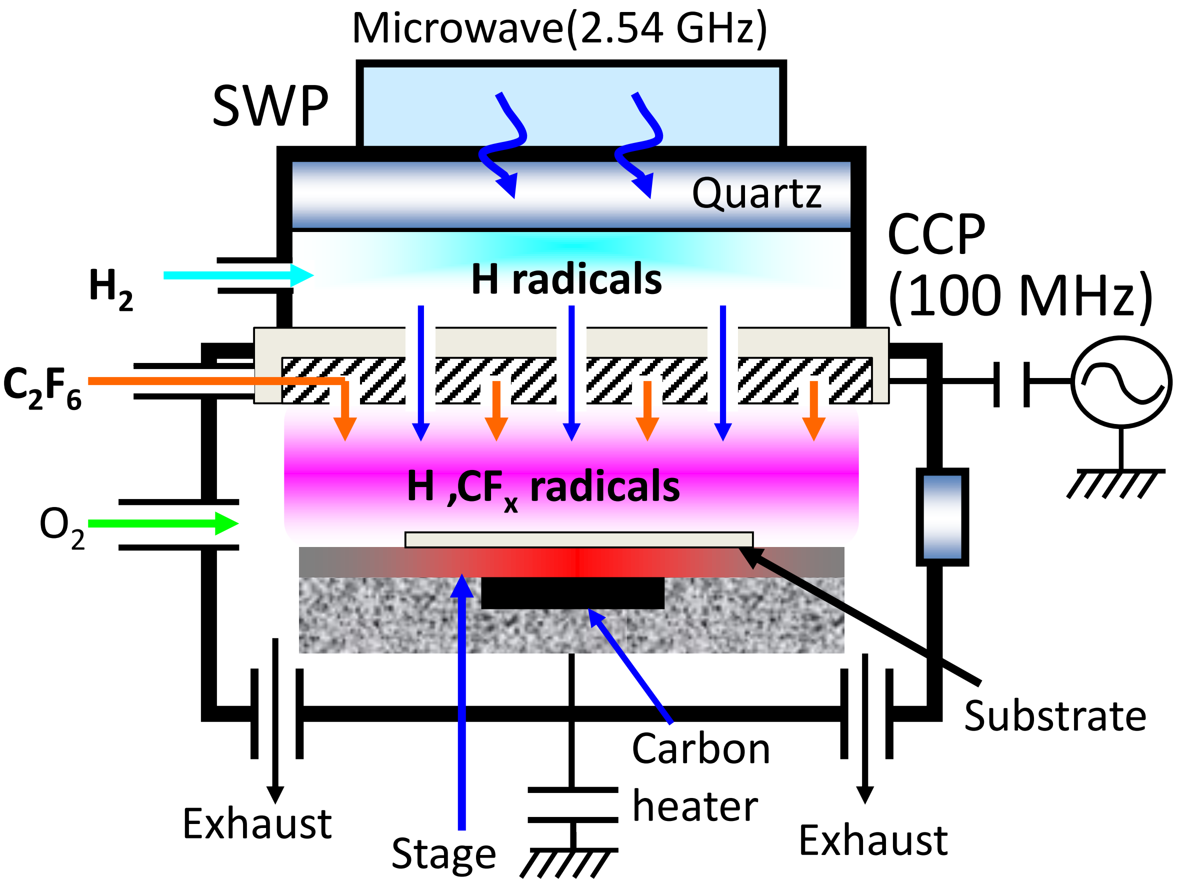
H : Vacuum Ultraviolet Absorption Spectroscopy

CF, CF_2, CF_3 : Appearance Mass Spectroscopy



Ratio of CF_3 radical to H atom could be an important factor to design CNWs the morphology.

Tandem Type Radical-Injection Plasma-Enhanced Chemical Vapor Deposition (RI-PECVD)



- Independent control of H and CF_x ,CH_x radicals using two plasma sources

Definition in this study

C_2F_6/H_2-CNWs

→CF-CNWs

CH_4/H_2-CNWs

→CH-CNWs

Growth conditions

Substrate: p-Si(100), 0.02 Ωcm

H_2: 100 sccm

C_2F_6 or CH_4 : 50 sccm

SWP power: 250 W

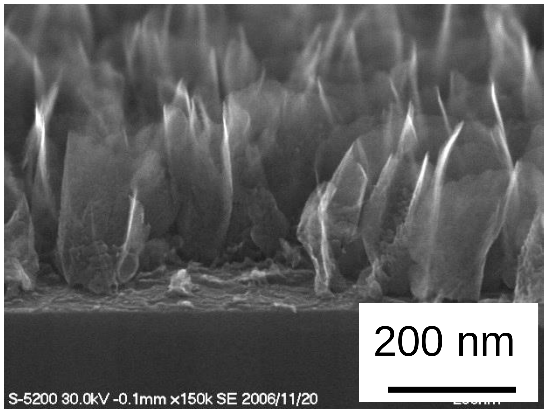
VHF power to : 270 W

Substrate temperature: ~600°C

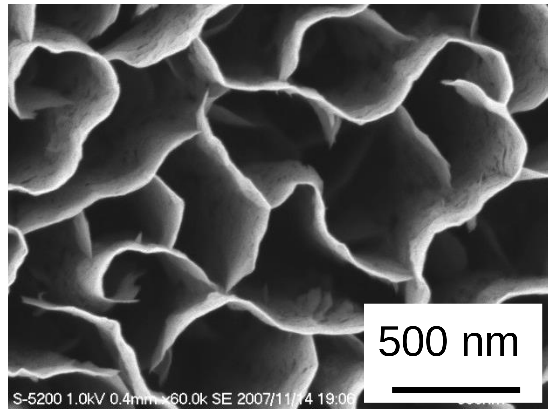
Total pressure: 80-160 Pa

Growth time: 30-170 min.

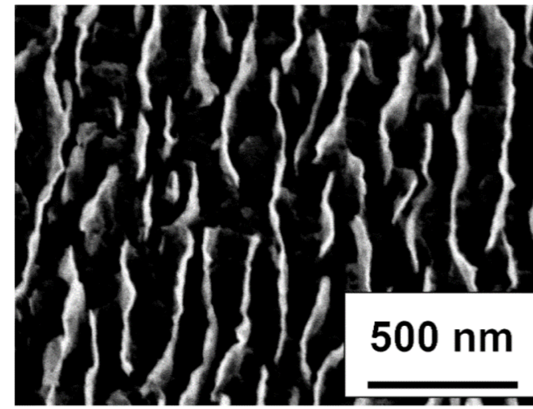
We can design a variety of Carbon Nanowalls by radical controlled plasma



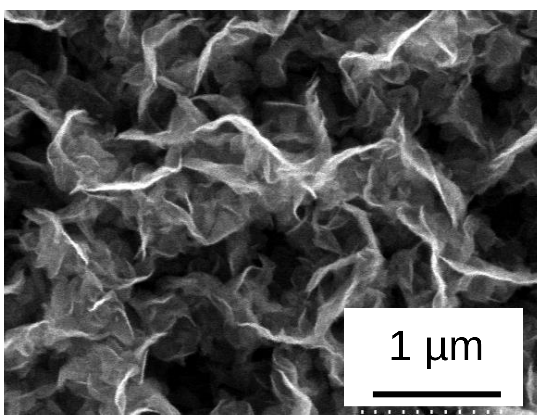
Isolated nanosheet



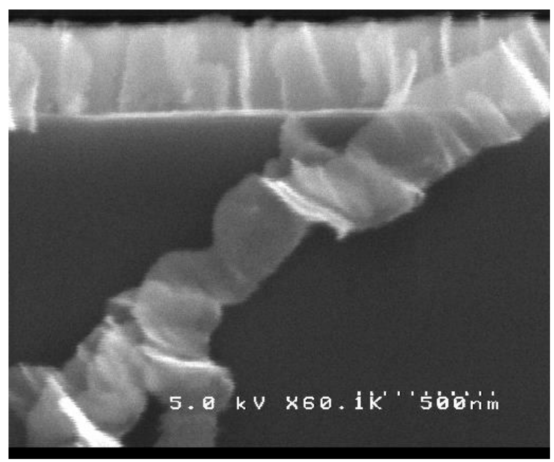
Maze-like wall



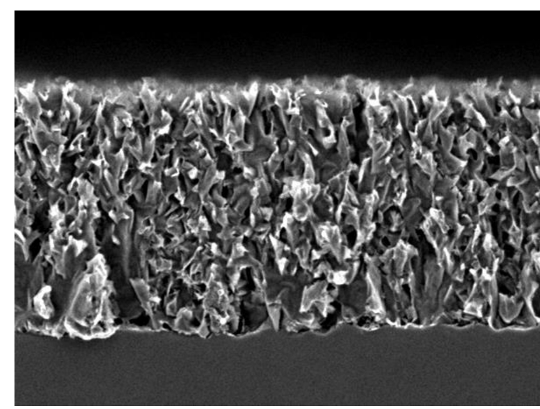
Aligned wall



Wavy

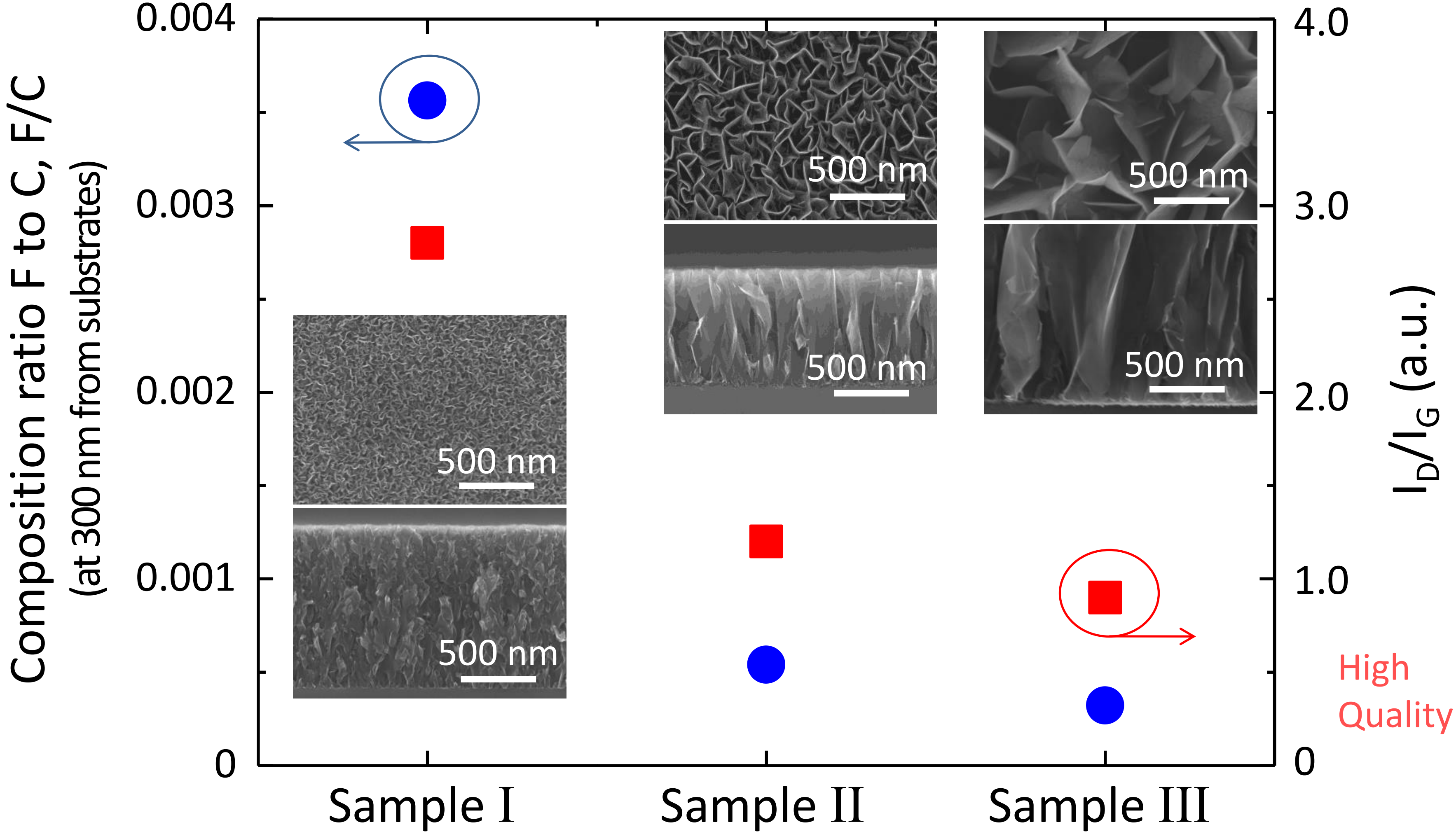


Vertical nano-ribon



Dense (porous film)

Fluorinated CNWs (CF-CNWs)
Composition ratio, crystallinity, and morphology



Plasma emission (OES): $CF_2/H\alpha = 1.4$

$CF_2/H\alpha = 1.0$

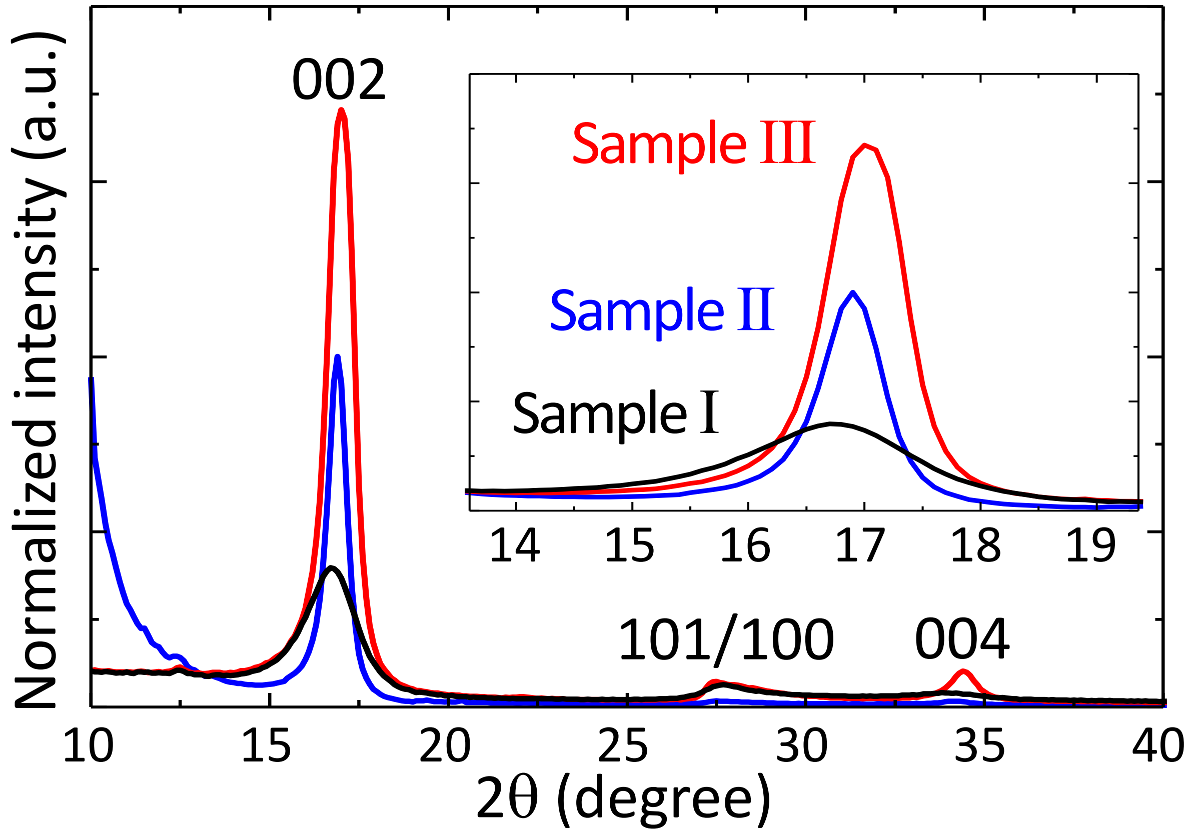
$CF_2/H\alpha = 0.5$

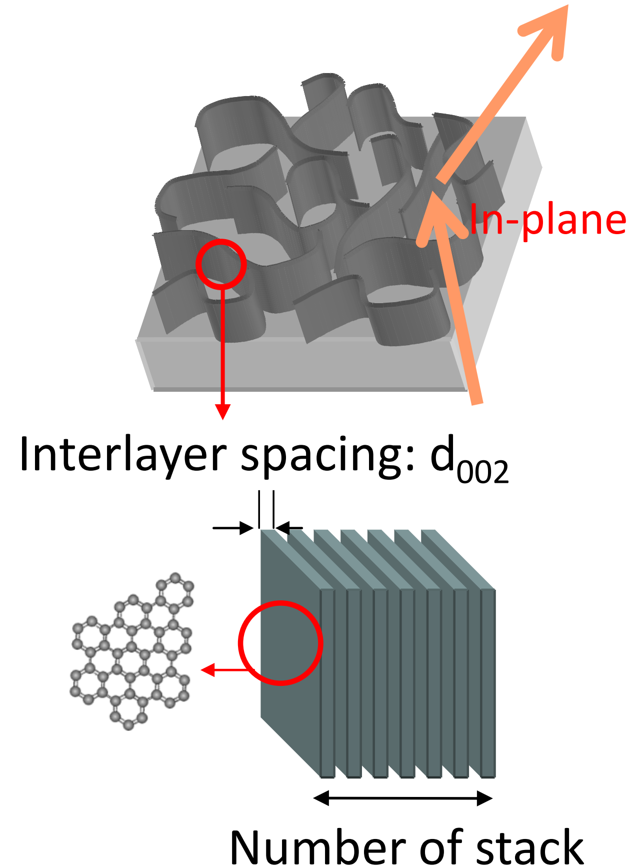
Synchrotron X-ray analyses at SPring-8

Synchrotron X-ray analyses
at SPring-8
(Super Photon ring-8 GeV)

X-ray photoelectron spectroscopy (XPS)	X-ray Absorption Spectroscopy (XAS)	Soft X-Ray Emission Spectroscopy (SXES)	X-ray diffraction (XRD)
↓	↓	↓	↓
Chemical bonding state	Electronic structure of conduction band	Energy band dispersion Local density of states	Crystalline structures

Interlayer spacing (d_{002}) and domain size (by SR XRD)





	d_{002} (nm)	Domain size (nm)
Sample I : (CF_2/Hα = 1.4)	0.344	3.3
Sample II : (CF_2/Hα = 1.0)	0.341	8.3
Sample III : (CF_2/Hα = 0.5)	0.339	6.0
Graphite	0.335	—

Interlayer spacing: *d*

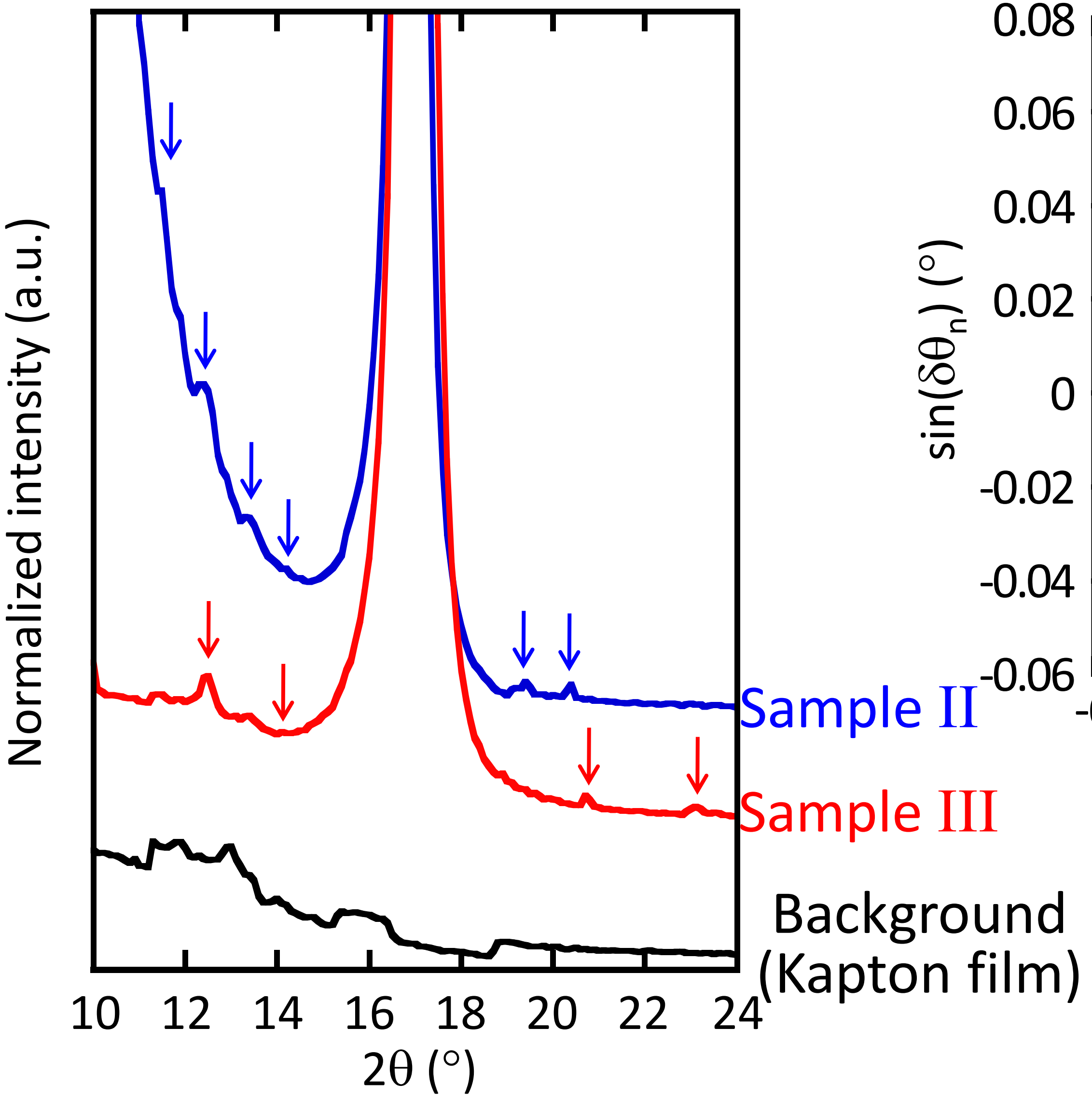
$\lambda = 2d\sin\theta$ (λ=1.00393 (Å))

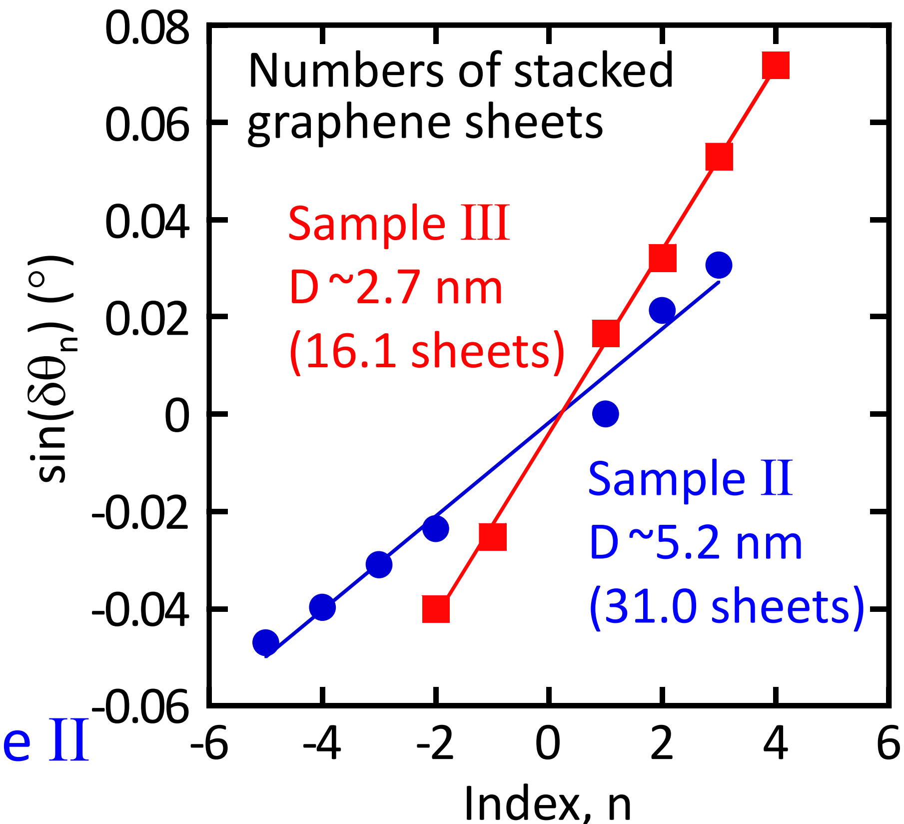
Shelar's formula

Domain size= $0.9\lambda / B \cdot \cos\theta_B$

(B: FWHM, θ_B : Bragg angle)

Numbers of stacked graphene sheets (by SR XRD)

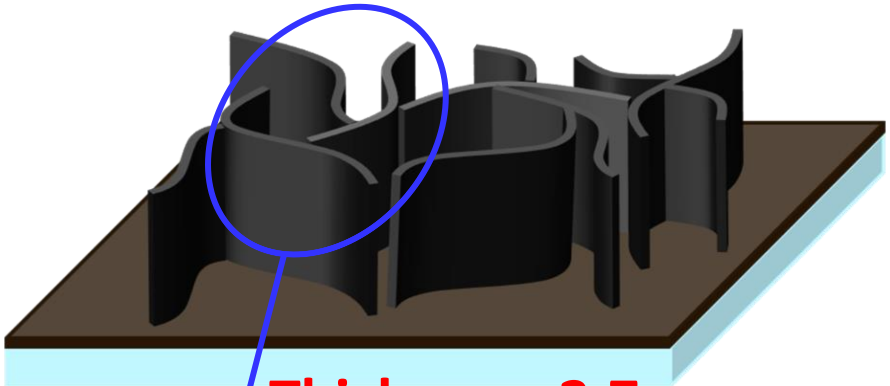


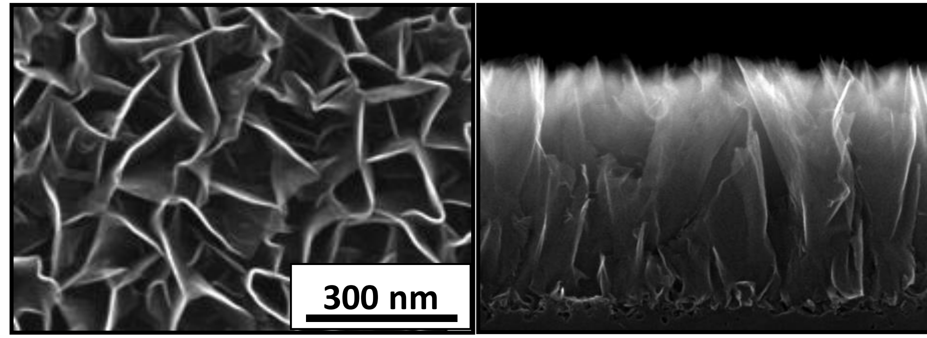


<u>Thickness of of stacked graphene sheets: *D*</u>

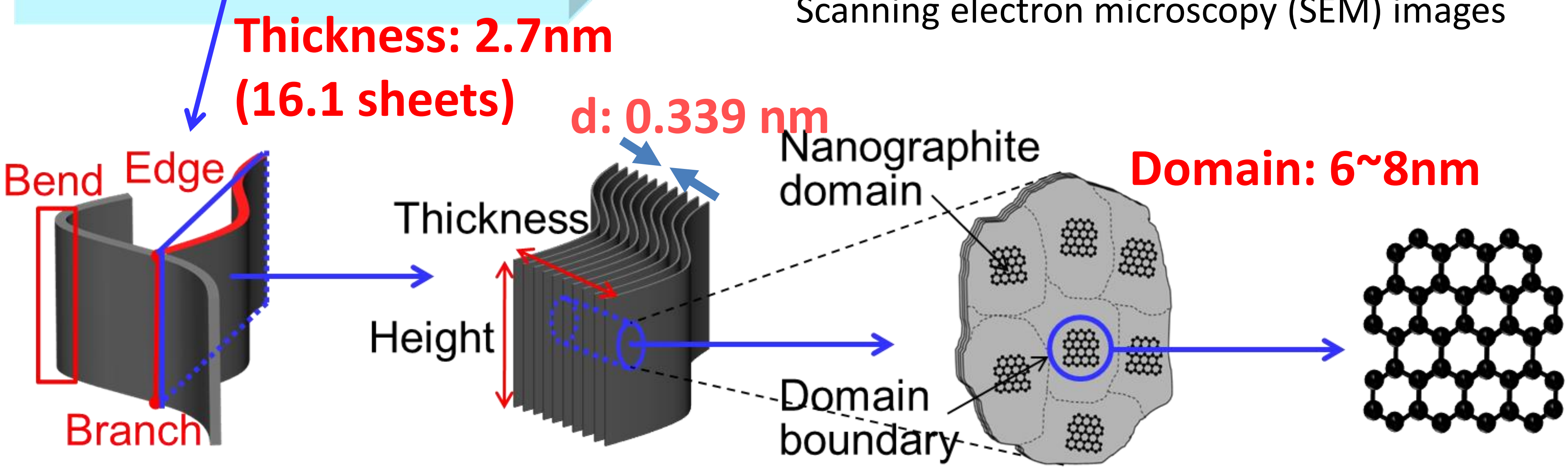
$$\lambda = \frac{2D}{n}\sin(\delta\theta_n)$$

Nano-Structures of Carbon Nanowalls (CNWs)





Scanning electron microscopy (SEM) images



Graphene nanostructures

CNW (graphene sheets)

Nanographite domain structure

Six-membered ring structure

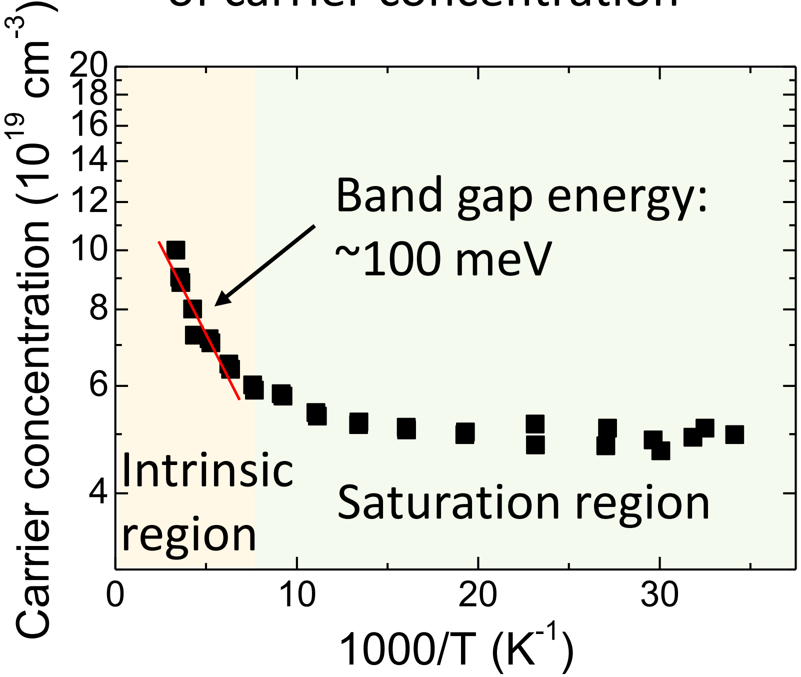
High-density edges and large surface area planes

Various defects and structural fluctuations

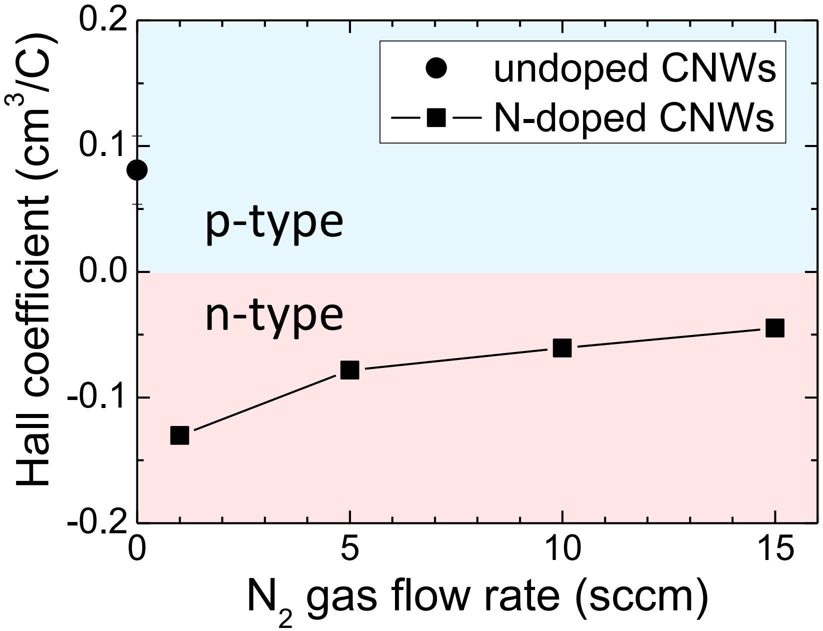
Impact on Electronic Properties of CNWs

ex. Electrical properties of CNWs (Hall effect measurements)

Temperature dependence of carrier concentration[1]



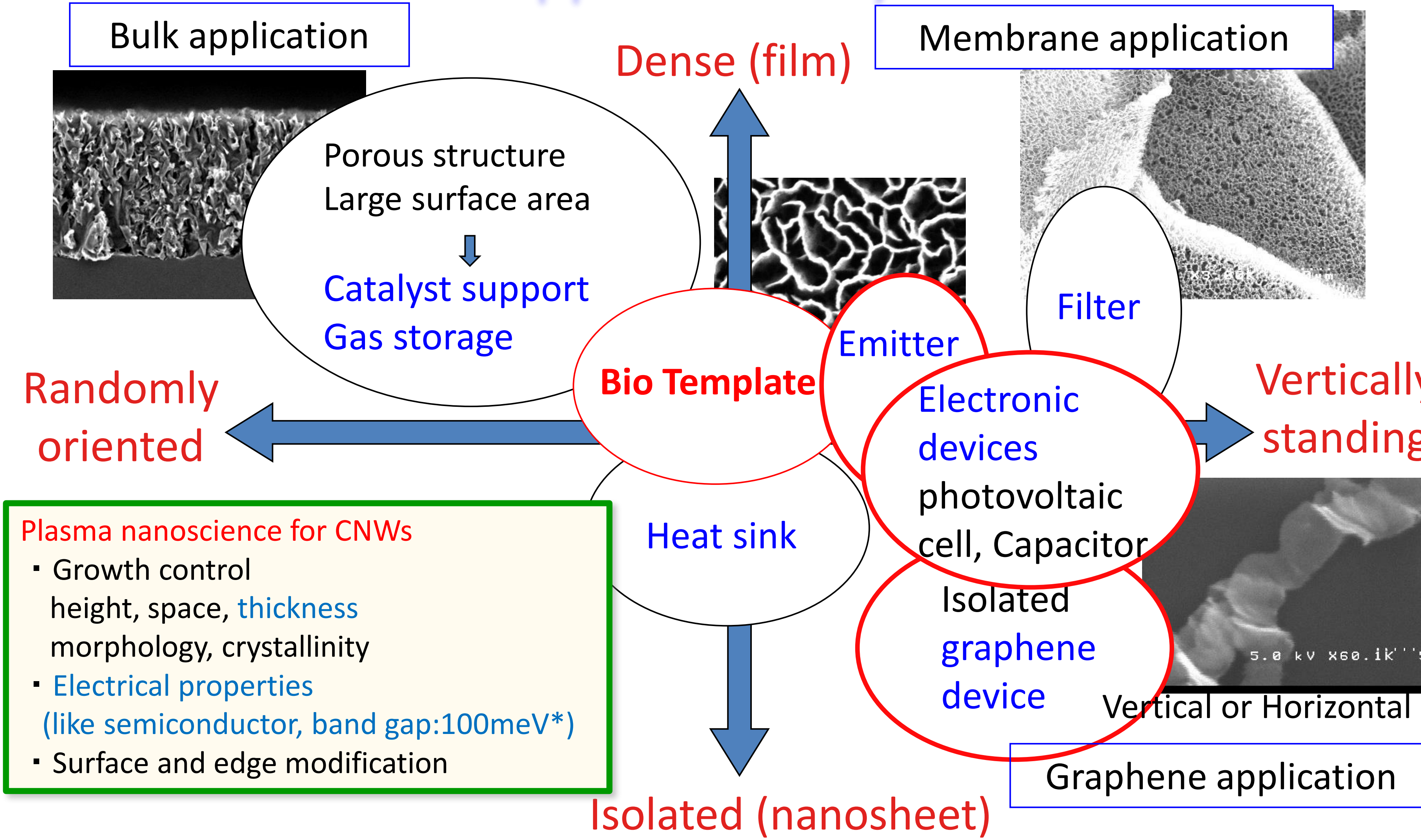
Change in Hall coefficient by nitrogen (N) doping[2]



Semiconducting properties

[1] H. Kondo, *et al.*, Appl. Phys. Lett. **99** 213110 (2011).
[2] W. Takeuchi, *et al.*, Phys. Status Solidi **207** 139 (2010).

Global Applications by CNWs



T. Machino, Appl. Phys. Express, pp.025001-1-025001-3 (2009)

K. Mase, APL, 98, pp. 193108-1:3 (2011) .

*W. Takeuchi, Phys. Status Solidi A 207, pp. 139-143 (2009).

*W. Takeuchi, APL, 8, pp. 123107-1:3 (2011).

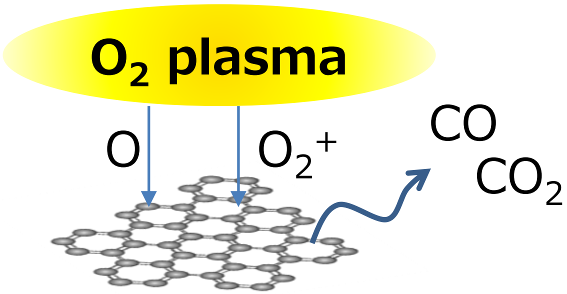
A Real time - TEM observation of etching of a "*conventional 2D graphene*" by remote oxygen plasma

.

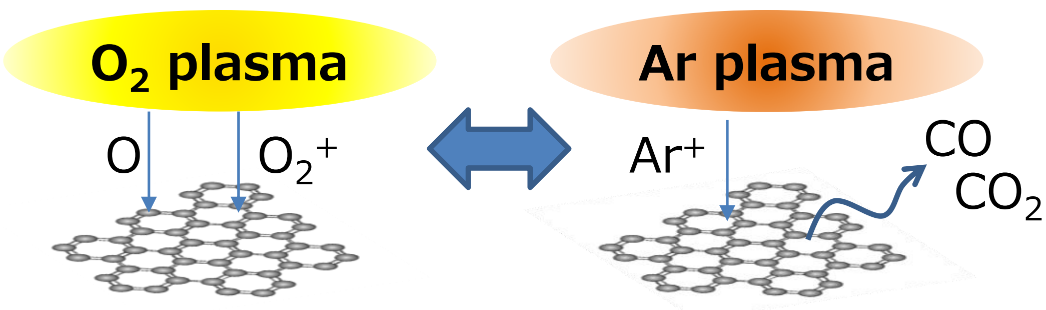
Seeing is believing!

Layer number control of graphene

- Plasma etching (O_2)[1,2]



- Cycle etching $O_2^+/O^+ \leftrightarrow Ar^+$[3]



Etching mechanisms:
Not clarified

In-situ analyses

- X-ray photoelectron spectroscopy(XPS)
- Electron spin resonance (ESR)
- Scanning tunneling microscopy (STM)
- Atomic force microscopy (AFM)
- Scanning electron microscopy (SEM)

Reaction process

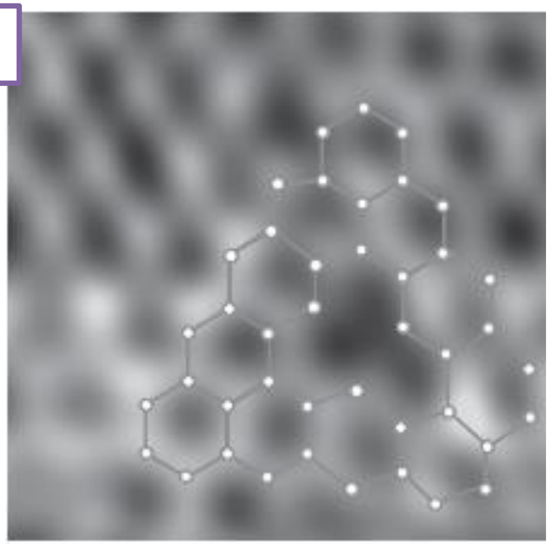
Atomic scale observation
Chemical binding state analysis

In-situ TEM
＋electron energy loss spectroscopy
(In-situ TEM-EELS)

[1] H. Fredriksson et al., Carbon **47**, 1335–1342 (2009).
[2] H. Al-Mumen et al., Nano Micro Lett. **6**, 116–124 (2014).
[3] K. S. Kim et al., Scientific Reports **7**, 2462 (2017).

In-situ TEM-EELS

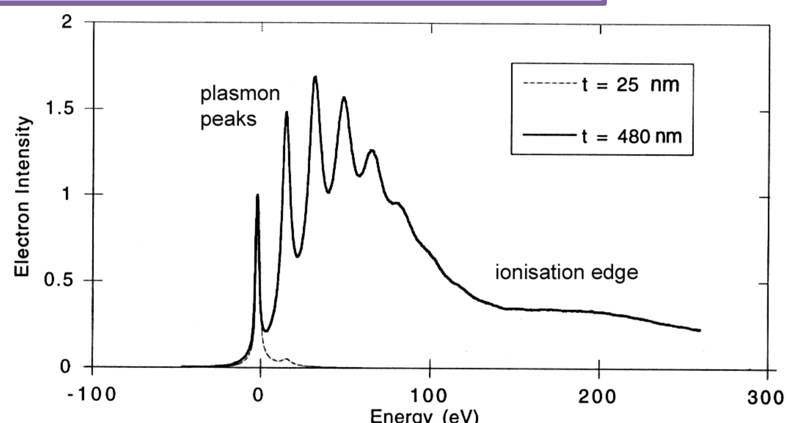
TEM image



[1]

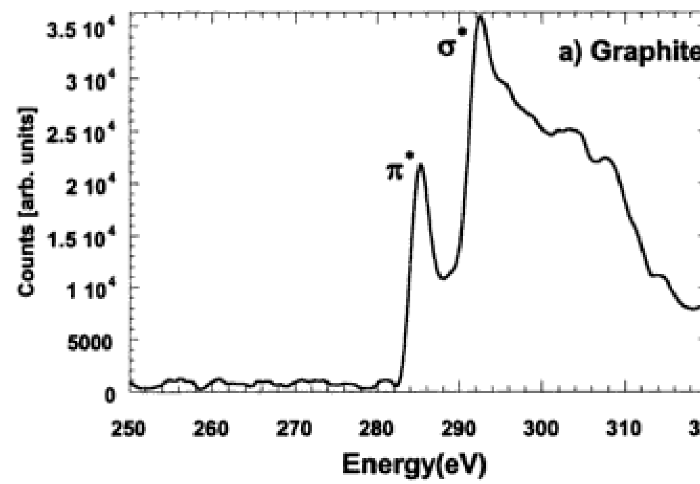
Electron diffraction pattern

Plasmon peak ⇒ Thickness



[2]

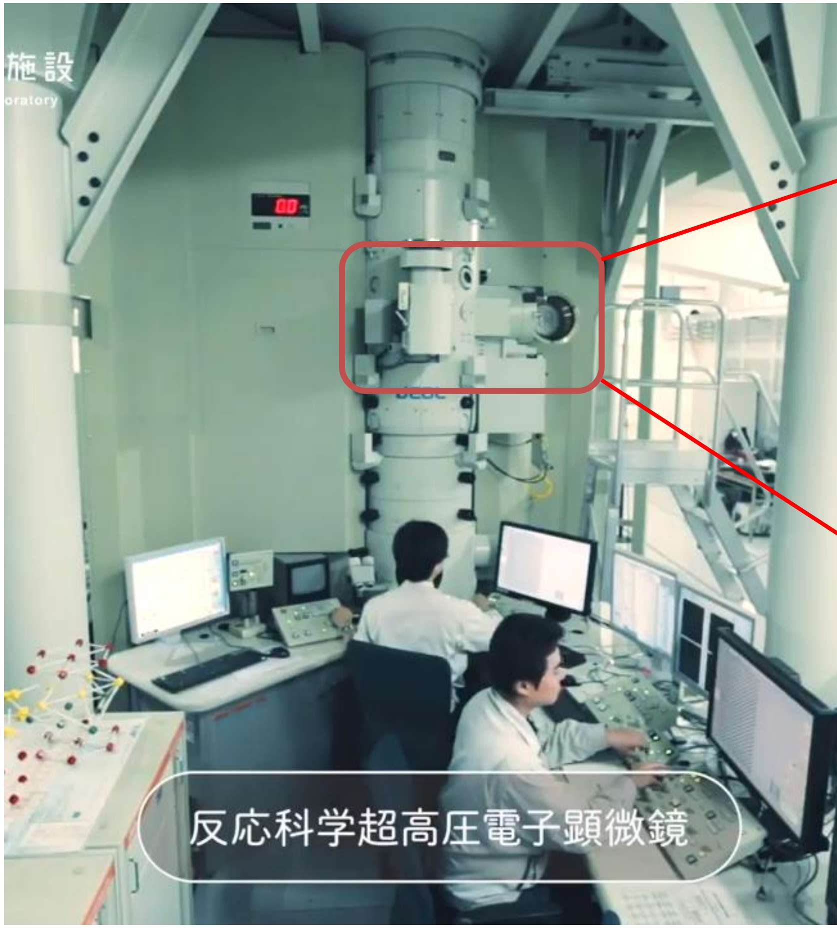
Core-loss peak ⇒ Binding states, Composition



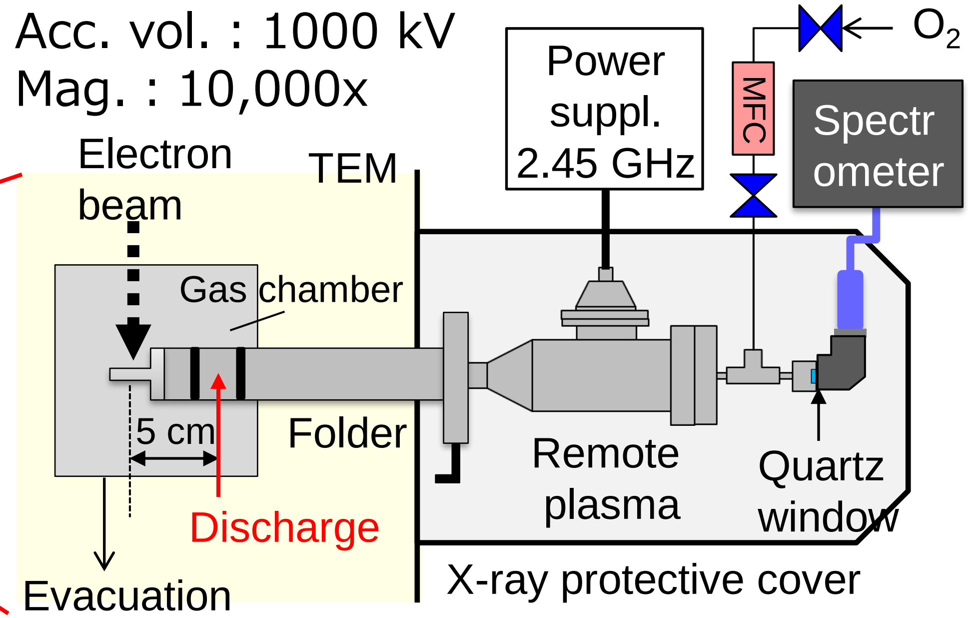
[3]

[1] M.H. Gass et al., Nat. Nanotechnol. **3**, 676 (2008).
[2] R.F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope,* Springer (2011).
[3] S. R. P. Silva, Properties of Amorphous Carbon, Inst of Engineering & Technology (2003).

Reaction science ultrahigh-voltage scanning transmission electron microscope

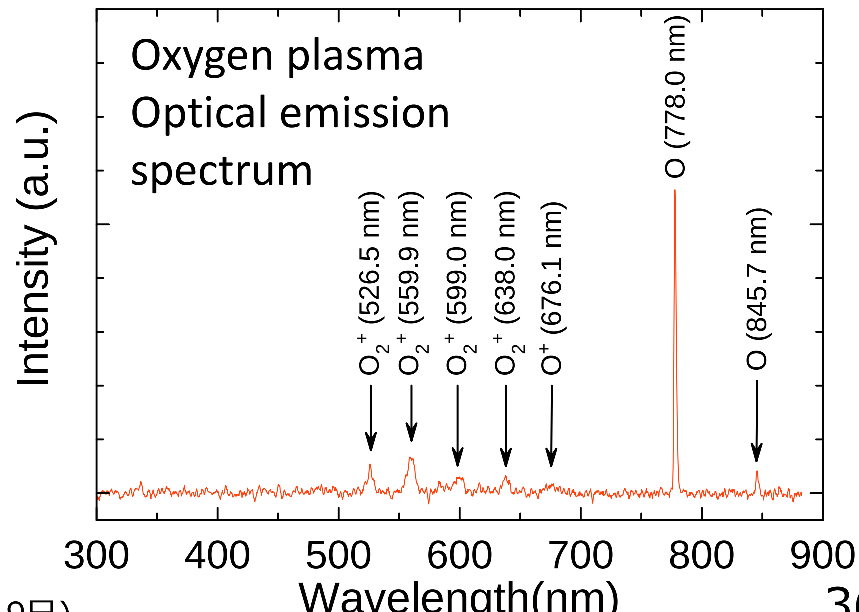


[1]



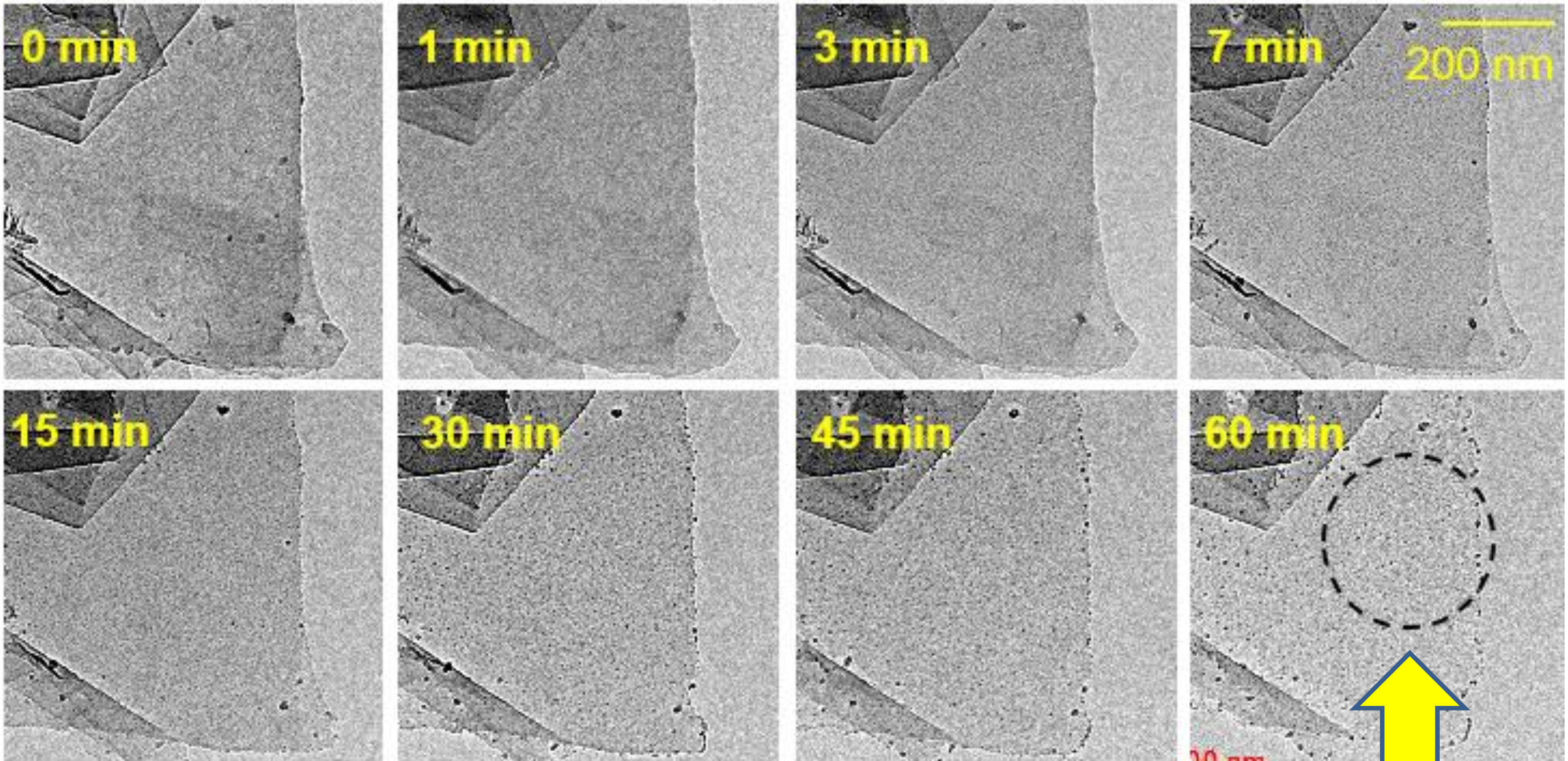
Discharge condition

O_2 1 sccm, 4.7 Pa, MW power 20 W



[1] http://hvem.nagoya-microscopy.jp/facility.html (2019年2月19日)

Real time observation of etching by remote oxygen plasma



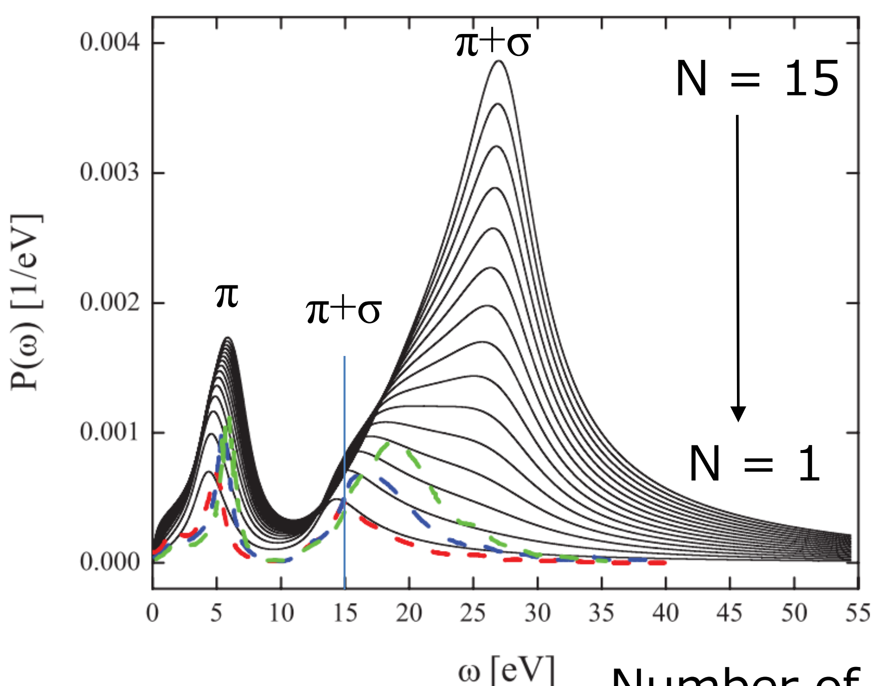
EELS analysis

Decrease of contrast by plasma irradiation

➡ Etching by oxygen atom irradiation

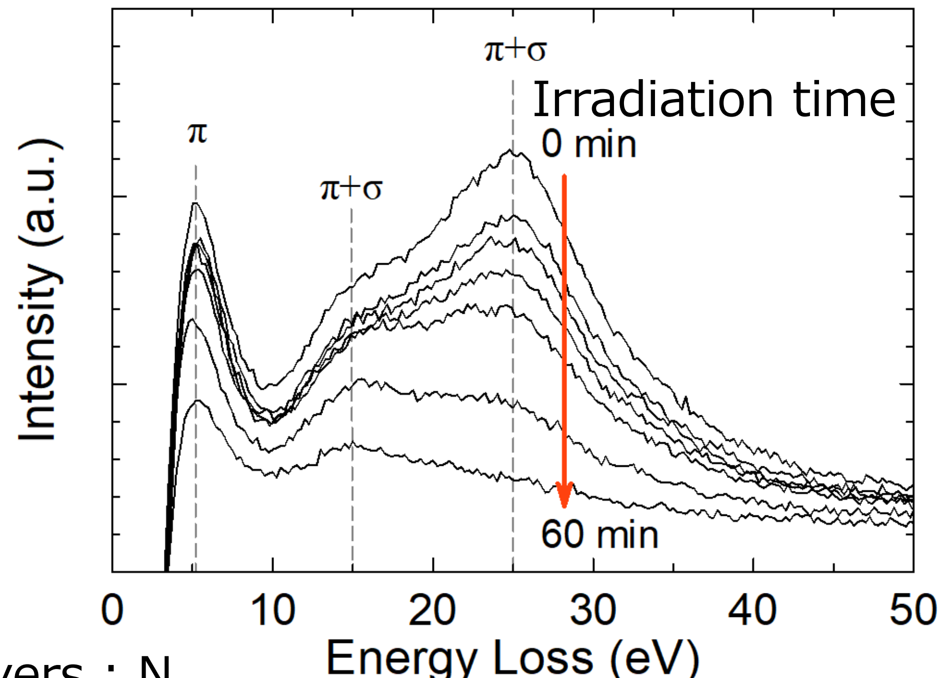
Estimation of layer number

Probability density; $P_N(\omega)$
vs. Energy loss; ω[1]



Number of layers ; N

Plasmon absorption (Experimental)



$[\pi+\sigma]_{15eV}$: Surface plasmon
$[\pi+\sigma]_{25eV}$: Bulk plasmon

Decrease of bulk components by plasma irradiation

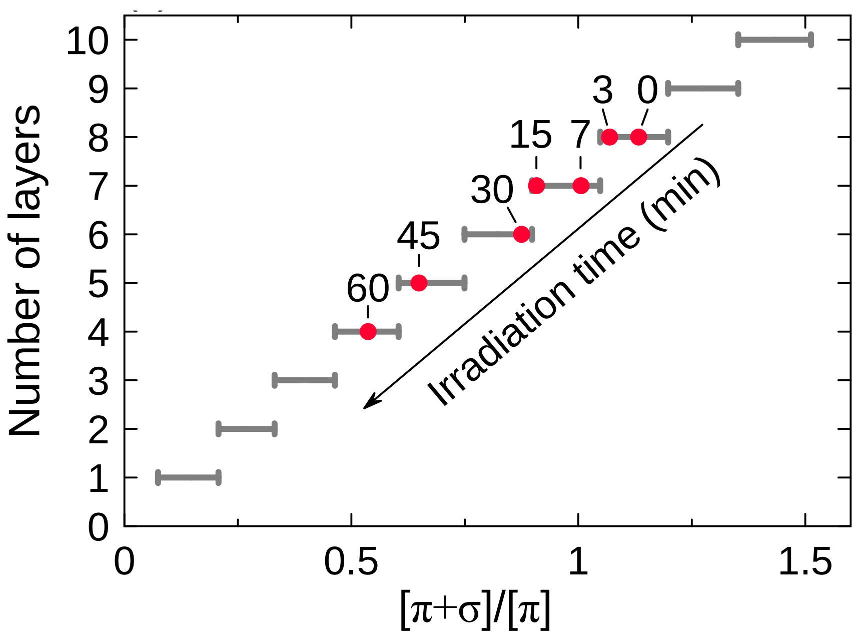
Decrease of $[\pi+\sigma]_{25eV}$ with layer number

Decrease of layer number

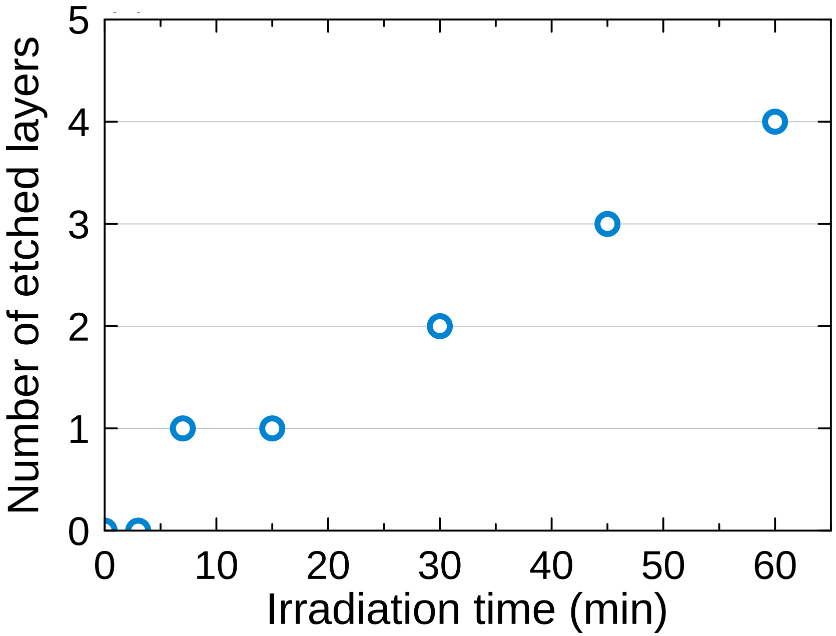
[1] V. Borka et al., Phys. Rev. B. **84** (2011) 155416.

Etching rate

Estimation of layer numbers based on intensity ratios of plasmon peaks



Number of etching layers
as a function of plasma irradiation time

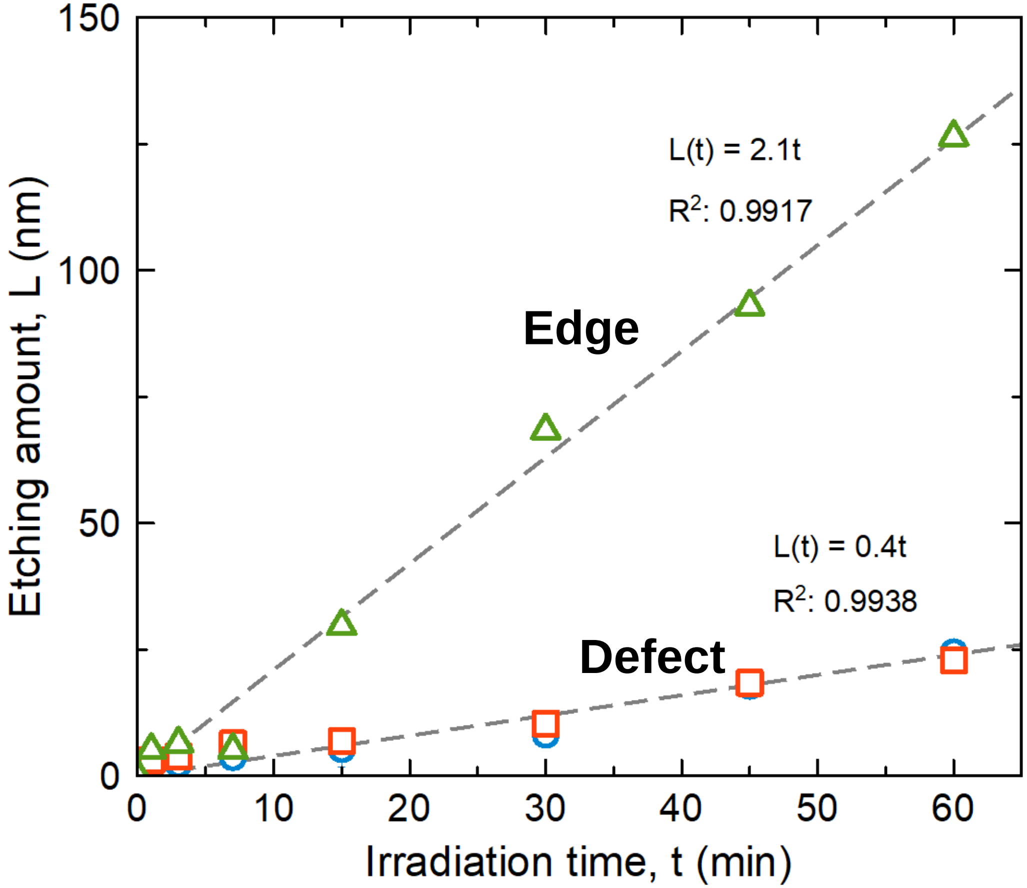


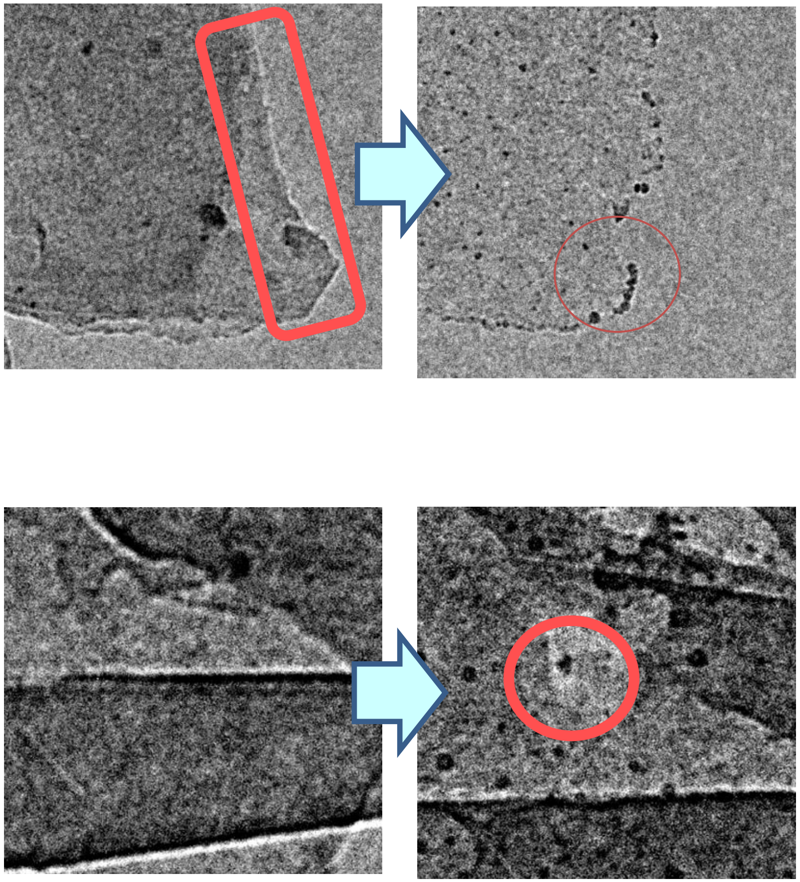
Remote oxygen plasma irradiation for 15 min

⇒ Etching of monolayer graphene

H. Sugiura et al., Carbon, 170, 93-99 (2020).

Etching on Plane, edge and defects of graphene





Edge：2.1nm/min
Defect：0.4nm/min、
Plane：1layer（0.335nm）/15min：0.0223nm/min

Sustainable Future ～ SDGs～

Global Problems
Energy, Food, Environment, Health, Mobility

Future Society
H_2 Society, Ubiquitous Society, Safety & Long Life Society

Social Innovation

Material & Device

Environment

Food Crisis

Medicine

Disruptive Innovations

Plasma Nanotechnology

Plasma Green Technology

Plasma Agriculture Fishery Technology

Plasma Medical Technology

Atomic Level Control

Self-organization

Programmed Processing

Engineering

Sociology

Bio-agriculture

Medicine

Interdisciplinary Science

Plasma Diagnostics

Plasma Data Base

Low Temperature Plasma Science

Plasma Design & Control

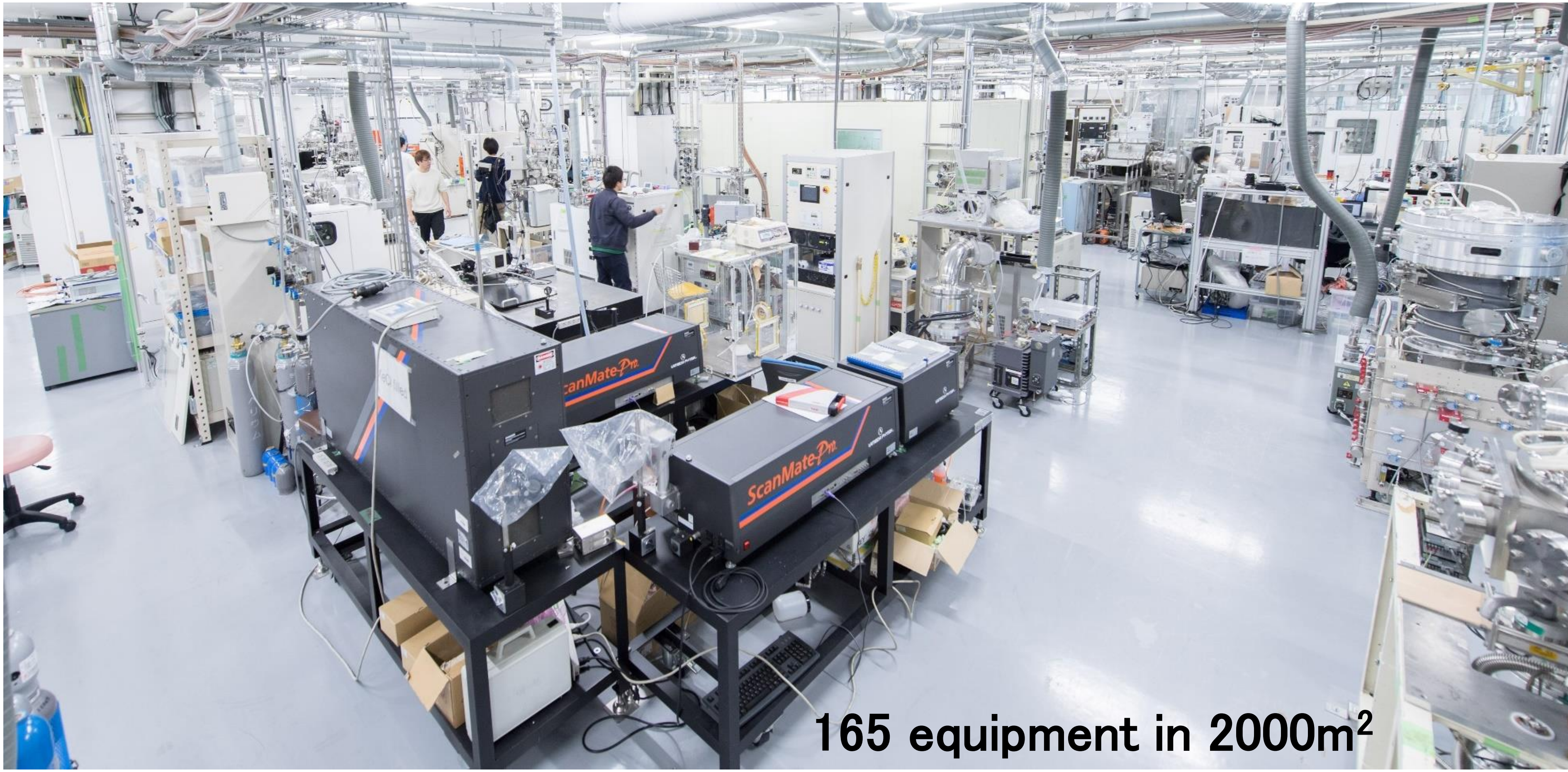
Center for Low-temperature Plasma Sciences Nagoya University (since 2019, April 1)

cLPS

National Joint Usage / Research Center

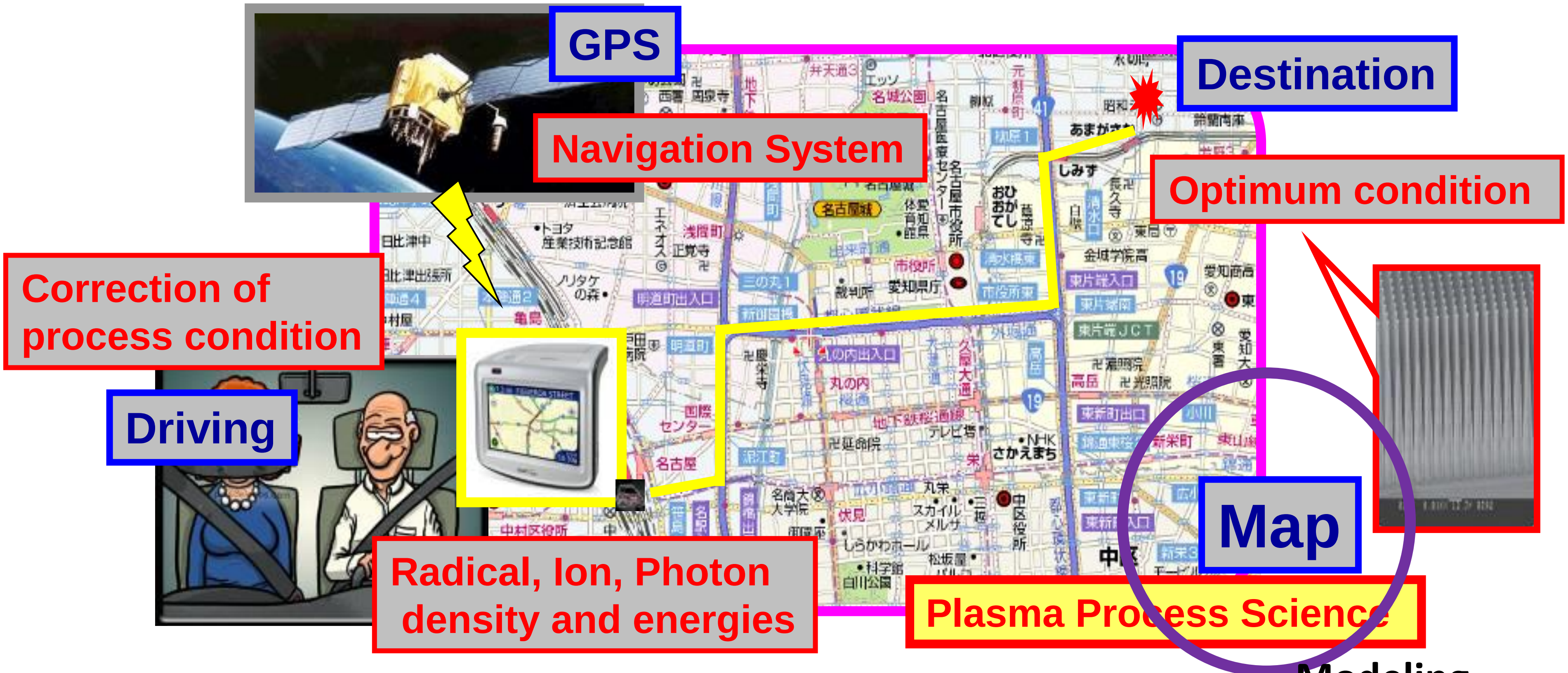
Plasma Science Platform

“Reliable scientific data set” for plasma informatics

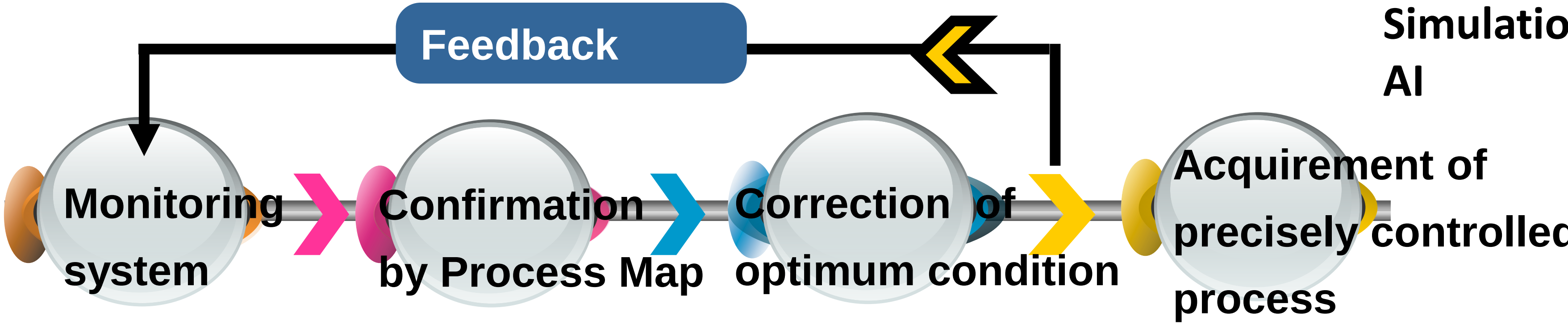


Real time monitoring / In situ monitoring
Time-evolution monitoring
Integration of big data which was analyzed by AI
Establishment of Plasma Sciences through a “global network”

Final Goal : Will We Ever Control Plasmas Based on Plasma Sciences?



Modeling
Simulation
AI



Acknowledgements

科研費
KAKENHI

This work was partly supported by a Grant-in-Aid for Specially Promoted Research (No. 19H05462).