Evolution of Plasma Nanoprocess

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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

Technological Singularity (AI more than the human race)

Industry Innovations

We are at a turning point in time.

III Era

Neuro Human Life Innovations

II Era

Plasma Material/Device towards IoT

I Era

Plasma Life Sciences

Thomson Reuters Database
Plasma Nanoprocesses for Future Innovations

Nano device Innovation

ULSI, Memory Mobile Phone, Display

Green Innovation

Energy Devices Solar Cell, Fuel Cell, LED, Battery

Life Innovation

Bio Device Medicine Healthcare Agriculture

Precise, Ultra-high Speed Processes based on Plasma Science

Energy Devices

Diagnostics

Modeling Simulation

Generation Control of Plasma

Programmed Processing (Self-management)

Atmospheric Pressure Plasma

In-Liquid Plasma

Ⅰ Era

Ⅱ Era

Ⅲ Era

“Plasma Informatics” with AI should be driven by obtaining reliable scientific data set (big data) for plasma nano-science.
Technology trends

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

**Trend of 10-Gb/s optical transceiver**

**Change in technology node for FET**

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

Important factors for etching (pattern size control)

Ion assist

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

Chemical reaction -> Arrhenius equation

\[
k = A e^{-\frac{E_a}{RT}}
\]

- \(T\) : 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.
(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$_x$H$_y$ 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

Integrated Monitoring System
Self judge, Self Control, Self Repair

Atom/Molecule Sensing System

Compact Radical Monitoring

Sub.Temp. Sensor
Film Monitoring Sensors
for the Thickness, Structure, composition, etc (in-situ FT-IR, Spectroscopic ellipsometer)

Plasma Reaction Space
radicals

Electrode

Optimum Process-Control System

Multi-channel Sensor Allay

Data Base
AI

Self judge, Self Control, Self Repair

Autonomic Controlled Nano-Production System
Experimental setup for etching of organic films

Gas: \( \text{H}_2 / \text{N}_2 = 75 / 25 \text{ sccm} \)
- 100 MHz power: 400 W
- 2 MHz power: 200 W (Directional etching)
- 0 W (Trimming)

Pressure: 2 Pa
Coolant temperature: 10, 50, 90°C

VUV absorption spectroscopy
For H and N radical densities

ACT-FD-LCI

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

• 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
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.
Etched feature of organic film depending on temperature

\[ \text{H / (H+N) = 0.52} \]

Etched profiles at 50 s

Slope \( \theta \): 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!
Trimming process was performed at a constant 100°C.
A new self-limited processing (Possibility of no-fluctuation in size)

Height: 200 nm  
Width: 35 nm

Height: 150 nm  
Width: 10 ~ 15 nm

Height: 130 nm  
Width: 8 ~ 13 nm

Self-limit
8 nm
To simulate chemical reactions on the side wall pattern by H and N radicals at 100°C

Analysis the organic surface treated by H₂/N₂ plasma by \textit{in-situ} XPS

Carbon / Nitrogen ratio

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

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

Thickenss (assumption): ~27 nm

~5 nm (Etching Stop)

Self-limit
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.

![Diagram of nano-patterning process](image)

- **N rich layer**
- **Etch**
- **CN molecular layer**
- **Self-limit**
- **Si substrate**

100°C, 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

Self-Organization

Top-view
Cross-sectional view
Carbon Nanowalls

Substrate
Thickness
Length
Height

Graphene sheet

Aspect ratio over 1000

2nm


28 patent registrations, 62 patent applications.
Self Organization Growth
By Plasma Nanoprocessing!

Ultrahigh Aspect Ratio over 400

Wall height and thickness (nm)

Growth time (hours)

Height

Space

Thicknss
Observation of early stage of CNW growth

Coverage with amorphous carbon layer

Onset of isolated nanosheets

Cross-sectional view

Amorphous carbon layer (10-30 nm)
Carbon Nanowall Growth Mechanism
Plasma Induced Self-organization Process

Ion
Active Site (Nucleation Site)
Amorphous Layer
Substrate

CF$_3$, CH$_x$

Ion
Radical
Ion
Radical
aggregation

Carbon nano-structure

Surface Migration

High Aspect Shadowing Effect

Vertical growth of graphene sheet
Ratio of \( \text{CF}_3 \) radical to \( \text{H} \) 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

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**Definition in this study**

- $\text{C}_2\text{F}_6/\text{H}_2$-CNWs → CF-CNWs
- $\text{CH}_4/\text{H}_2$-CNWs → CH-CNWs

**Growth conditions**

- Substrate: p-Si(100), 0.02 Ωcm
- $\text{H}_2$: 100 sccm
- $\text{C}_2\text{F}_6$ or $\text{CH}_4$: 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.
Fluorinated CNWs (CF-CNWs)
Composition ratio, crystallinity, and morphology

Sample I
Plasma emission (OES): $\text{CF}_2/\text{H}\alpha = 1.4$

Sample II
$\text{CF}_2/\text{H}\alpha = 1.0$

Sample III
$\text{CF}_2/\text{H}\alpha = 0.5$
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)

Interlayer spacing: $d$

\[ \lambda = 2d \sin \theta \quad (\lambda = 1.00393 \text{ Å}) \]

Shelar’s formula

\[ \text{Domain size} = 0.9 \frac{\lambda}{B \cdot \cos \theta_B} \]

(B: FWHM, $\theta_B$: Bragg angle)

### Table

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d_{002}$ (nm)</th>
<th>Domain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample I: (CF$_2$/H$\alpha$ = 1.4)</td>
<td>0.344</td>
<td>3.3</td>
</tr>
<tr>
<td>Sample II: (CF$_2$/H$\alpha$ = 1.0)</td>
<td>0.341</td>
<td>8.3</td>
</tr>
<tr>
<td>Sample III: (CF$_2$/H$\alpha$ = 0.5)</td>
<td>0.339</td>
<td>6.0</td>
</tr>
<tr>
<td>Graphite</td>
<td>0.335</td>
<td>—</td>
</tr>
</tbody>
</table>
Numbers of stacked graphene sheets (by SR XRD)

Normalized intensity (a.u.)

2θ (°)

10 12 14 16 18 20 22 24

Background (Kapton film)

Sample II

Sample III

Sin(δθ, °)

Index, n

Sample II

D ~ 5.2 nm

(31.0 sheets)

Sample III

D ~ 2.7 nm

(16.1 sheets)

Thickness of stacked graphene sheets: $D$

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

Data 20 3:35:44 2010/03/19

$\sin(\delta \theta)$

$y = -0.0017946 + 0.0096323x$  $R = 0.99069$

$y = -0.0039655 + 0.018859x$  $R = 0.99925$
Nano-Structures of Carbon Nanowalls (CNWs)

High-density edges and large surface area planes
Various defects and structural fluctuations

Graphene nanostructures

Graphene sheets

CNW (graphene sheets)

Nanographite domain structure

Nanographite domain

Thickness: 2.7 nm (16.1 sheets)

d: 0.339 nm

Domain: 6~8 nm

Six-membered ring structure

Scanning electron microscopy (SEM) images

300 nm
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\(^{[2]}\)

- **Band gap energy:** \(~100\) meV

- **Intrinsic region**
- **Saturation region**

- **p-type**
- **n-type**

Semiconducting properties

Global Applications by CNWs

- Bulk application
- Membrane application
- Dense (film)
- Isolated (nanosheet)
- Vertically standing
- Randomly oriented

- Porous structure
- Large surface area
- Catalyst support
- Gas storage

- Bio Template
- Emitter
- Electronic devices
- Photovoltaic cell, Capacitor
- Isolated graphene device

- Heat sink

- Filter

- Plasma nanoscience for CNWs
  - Growth control: height, space, thickness, morphology, crystallinity
  - Electrical properties: like semiconductor, band gap: 100meV*
  - Surface and edge modification

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 ($O_2$)$^{[1,2]}$

\[
O_2 \text{ plasma} \quad O \quad O_2^+ \quad CO \quad CO_2
\]

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

\[
O_2 \text{ plasma} \quad O \quad O_2^+ \leftrightarrow Ar^+ \quad CO \quad CO_2
\]

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)

In-situ TEM-EELS

Oxygen plasma Optical emission spectrum

Discharge condition

O₂ 1 sccm, 4.7 Pa, MW power 20 W

Real time observation of etching by remote oxygen plasma

Decrease of contrast by plasma irradiation

Etching by oxygen atom irradiation

EELS analysis
Estimation of layer number

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

$N = 15$

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

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

Plasmon absorption (Experimental)

Decrease of bulk components by plasma irradiation

Decrease of layer number

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**
- $2.1 \text{nm/min}$

**Defect**
- $0.4 \text{nm/min}$

**Plane**
- 1 layer ($0.335 \text{nm}$) / 15 min: $0.0223 \text{nm/min}$
Sustainable Future ～ SDGs～

Global Problems
Energy, Food, Environment, Health, Mobility

Future Society
H₂ 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

Self-organization
Plasma Data Base

Programmed Processing
Atomic Level Control
Engineering
Society
Bio-agriculture
Interdisciplinary Science
Medicine

Low Temperature Plasma Science

Interdisciplinary Science: Plasma Design & Control
Center for Low-temperature Plasma Sciences
Nagoya University (since 2019, April 1)

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?

- GPS
- Destination
- Navigation System
- Optimum condition
- Correction of process condition
- Driving
- Map
- Radical, Ion, Photon density and energies
- Plasma Process Science
- Modeling
- Simulation
- AI
- Monitoring system
- Confirmation by Process Map
- Feedback
- Correction of optimum condition
- Acquisition of precisely controlled process
Acknowledgements

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