HOW CAN PLASMAS BUILD CARBON NANOSTRUCTURES?

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Carbon Nanostructures: Timeline

1985-Fullerene

1991-Carbon nanotube

1997-Carbon

2002- Carbon Nanowall

2004-Graphene

Graphene : Constituent of Carbon Nanostructures

Carbon Nanowalls (CNWs) or Graphene nanowalls (GNWs)
Vertically aligned 2D carbon nanosheets

Why Carbon Nanowalls...?

- Catalyst support
- Electrochemistry
- Template for growing other types of materials
- Field electron emitters
- Electronic devices
- Hydrophobic coating
- Heat sink
- Filter
- Electric double layer capacitor
- Nanoimprint

Why Plasma-processing Techniques..?


❖ Large scale growth with selected properties
❖ Control in ordering/patterning
❖ Rapid production and fast processing
❖ Easier and safer
Plasma-assisted Synthesis Methods

- **Bottom-up approach**
  - Hydrocarbon/Fluorocarbon gas sources
  - Plasma interaction, deposition-nucleation and growth
  - Plasma Enhanced Chemical Vapor Deposition (PECVD)

- **Top-down approach**
  - Solid/Liquid carbon precursor
  - Plasma treatment on the precursor and growth
  - Plasma treatment on honey

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Plasma Treatment On Solid/Liquid Carbon Sources

- Carbon containing hydrogels: resorcinol-formaldehyde, cellulose hydrogel, phenol-formaldehyde
- Ar, H₂ gas
- Elevating temperature, dissociation into different radicals, etching of amorphous phase
- Carbon nanowall/nanostructures with uniform morphology and inter layer spacing
• Vertical growth of CNWs (Currently reported maximum ~ 300nm)
• Atomically thin edges, controlled spacing, and excellent height uniformity
Plasma Enhanced Growth of CNWs - Mechanism

Carbon radicals

Plasma source
HC/FC gases

Plasma induced defects on the substrate surface

Migration
Ion bombardment, adsorption, dissociation
Reaction

Carbon dimer
CH/CF

Monolayer growth
Nucleation
Termination

GROWTH

n(C_xH_y/C_xF_y) → xC_2 + yCH/CF + H/F

Nucleation and coalescence

Termination (α-C with H/F radicals)
Discharge Parameters

Finding optimum discharge parameters for the high yield growth

Different plasma power

CH$_4$ concentration
d) 10%, e) 40%, f) 100%

Different H$_2$/CH$_4$ flow rate ratios: (a) 30, (b) 15, (c) 10, (d) 6, (e) 4, (f) 1sccm
Substrate Temperature and Growth Time

Enhance the thermal stability of CNWs

Different growth temperatures: 630 °C, 730 °C, 830 °C.


Attaining the growth of CNWs @ low-temperature and short-time period with high quality
Effect of Pressure

Control the pressure, synthesize CNWs with uniform morphology, high orientation and larger interlayer spacing

**Lower plasma pressure**
- ✓ Higher electron energy
- ✓ Increasing ionization rate
- ✓ A low growth rate
- ✓ Higher vertical orientation

**Higher plasma pressure**
- ✓ Larger volume of feedstock gas input
- ✓ Electron energy decreased
- ✓ The massive production
Simulations - Formation of Vertically Oriented Graphenes: What are the Drivers of Growth?

We build a multi-scale, multi-factor model which was thoroughly verified by comparison with a large massive of experimental data to ensure a significant chemical and physical insight into the processes that determine nucleation, growth and structure formation of vertically-aligned graphenes from the case of plasma.

The leading role of surface diffusion fluxes, rather than direct influx from gas phase, was confirmed with the ion bombardment being a key factor ‘switching’ the growth modes by generating surface defects and hence, increasing the surface adsorption energy. Thus, the hydrocarbon radicals generated on a substrate due to the bombardment diffuse to the nanoflakes and catalyze the reactions, and serve as the primary source of material to build the nanoflakes.
The prepared substrates are loaded into the chamber of plasma reactor where the nanoflakes are nucleated on catalyst particles and then grow in the ion and atom flux. Schematic of the mechanisms and reactions involved in vertical graphene growth. Motion of species involved into the reactions about the surface of growing graphene flake (a); list of chemical reactions taken into account in the model (b); schematic of the reactions (c); and diagram of the energy levels (d). Substrate may be externally heated by the use of heating coil, or heated directly by the plasma.
The ion bombardment changes the adsorption mechanism on the substrate where the methane molecules (primary source of CHx radicals) adsorb, from the physical sorption (~ 0.5 eV) to the chemical sorption (~ 1-2 eV), to generate the large amount of the radicals on the surface at the elevated temperatures. The radical can diffuse along the surface layer, and can be adsorbed on the GNF flat side or sharp edge during the diffusion, at that the adsorption energy is changed from $\varepsilon_{aCHX}(\alpha)$ to $\varepsilon_{aCHX}(S)$ or $\varepsilon_{aCHX}(E)$, respectively. If the radical is adsorbed on the high-defect GNF edge, the adsorption energy is increased:

$$\varepsilon_{aCHX}(\alpha) \rightarrow \varepsilon_{aCHX}(E),$$

and the radical can diffuse along the edge with low probability of evaporation or transition to the side surface of the GNF sheet ($\varepsilon_{aCHX}(G) \gg \varepsilon_{aCHX}(S)$), see Fig. 1.

Furthermore, the model implicates several features:

(i) The nanoflakes morphology was explained by the difference between the energy of the physical sorption $\varepsilon_{aCHX}(S)$ on the defect-free flat surface of nanoflake, and the energy $\varepsilon_{aCHX}(E)$ of the chemical sorption on the defected edges of the GNF. The GNF grow when CHx radical is struck by ion at the diffusion from the GNF bottom to the top, and the carbon atom is released.

(ii) (As suggested by a number of researchers,14,29 the electric field on the exposed sharp edges of the nanoflakes is taken into account when describing the GNF growth. Strong enhancement of the electric field by sharp edges of a nanoflake plays a vital role in the GNF growth, since it intensifies the reactions by order of a magnitude at the ion focusing.

(iii) The diffusion of radicals from the substrate to the GNF top and the growth of the GNF in width depend on the ion current density $j_{IR}$ to the side, while the nanoflake growth in height depends on the ion current density $j_{IR}$ to the top; a re-distribution of the densities occurs at the nanoflakes growth.

(iv) The current densities to the side and top edges of the nanoflake change during the growth because of shielding of the nanoflakes side edge by the neighboring nanoflakes after the GNF array grows high.
Big data, i.e., large volume of information obtained from the multiscale multifactor model allows comprehensive analysis of the graphene formation and growth as a function of all essential parameters and processes in plasma.
Growth kinetics

GNF length on time under various growth conditions. \( j_{il} \) was considered a parameter, and calculated for various types of plasma discharge based on the experimental data. Comparison with experimental data shows that the ion bombardment results in changing the ion-stimulating diffusion to ion mixing mode. Non-linear growth with saturation is explained by a dependence of the ion current densities \( j_{il} \) and \( j_{ir} \) on time for the particular experiment.
Time evolution of a GNF shape at $j_0 = 0.41$ A/m$^2$, $P_{CHx} = 1300$ Pa, $T_s = 1000$ °C. The GNF shape evolves from a rectangular with a height to width ratio of about unity at the initial stages of growth (a), to a ribbon-like structure of limited height (~6 μm) (b). Experimental bars correspond to the results obtained by Krivchenko et al.$^{18}$ In the calculations the non-linear fit of $j_iL_jiR$ is assumed. (c) GNF growth rate on density of ion current, total gas pressure is a parameter.
On the experimental side ...
CH-CNWs  Experimental

CF-CNWs  Experimental

RI-PECVD system  
(Radical Injection Plasma Enhanced CVD)

- CH$_4$ : 100 sccm H$_2$ : 50 sccm
- Substrate : SiO$_2$
- Working pressure : 1 Pa
- Temperature : 600°C
- SWP power : 400 W
- CCP power : 300 W

Gas flow rates
H$_2$ : 100 sccm C$_2$F$_6$ : 50 sccm
Pressure : 133 Pa
Substrate temperature : 630°C
Microwave power : 250 W
VHF power : 250 W
Growth time : 40 min
**CH-CNWs** SEM images

**CF-CNWs 1**

**CF-CNWs 2**
**CH-CNWs Raman spectrum**

- D band $- 1328 \text{ cm}^{-1}$
- G band $- 1584 \text{ cm}^{-1}$
- D' band $- 1620 \text{ cm}^{-1}$

**CF-CNWs**

- 2D band $- 2685 \text{ cm}^{-1}$
- D+G band $- 2935 \text{ cm}^{-1}$
- 2D' band $- 3230 \text{ cm}^{-1}$
Different spacing between CNW

Process conditions and results of analyses of both principal tested CNWs (100 nm) and CNWs (300 nm).

<table>
<thead>
<tr>
<th></th>
<th>100</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average gap between each CNWs [nm]</td>
<td>100</td>
<td>300</td>
</tr>
<tr>
<td>Average height of CNWs [nm]</td>
<td>650</td>
<td>970</td>
</tr>
<tr>
<td>Conductivity [S/cm]</td>
<td>38</td>
<td>76</td>
</tr>
<tr>
<td>Process pressure [Pa]</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Substrate temperature [°C]</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>SWP power [W]</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>CCP power [W]</td>
<td>100</td>
<td>500</td>
</tr>
<tr>
<td>H₂ [sccm]:CH₄ [sccm]</td>
<td>50:100</td>
<td>50:100</td>
</tr>
<tr>
<td>Growth time [min]</td>
<td>60</td>
<td>10</td>
</tr>
</tbody>
</table>
Differences between CNW

$I_D/I_G$, $I_{D'}/I_G$, $I_{2D}/I_G$ ratios and the position of peaks of Raman spectra for both tested CNWs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_D/I_G$</th>
<th>$I_{D'}/I_G$</th>
<th>$I_{2D}/I_G$</th>
<th>$I_D$  [cm$^{-1}$]</th>
<th>$I_G$  [cm$^{-1}$]</th>
<th>$I_{D'}$ [cm$^{-1}$]</th>
<th>$I_{2D}$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNWs - 100 nm</td>
<td>2.29</td>
<td>0.91</td>
<td>0.40</td>
<td>1357</td>
<td>1597</td>
<td>1624</td>
<td>2693</td>
</tr>
<tr>
<td>CNWs - 300 nm</td>
<td>2.04</td>
<td>0.84</td>
<td>0.45</td>
<td>1334</td>
<td>1581</td>
<td>1607</td>
<td>2684</td>
</tr>
</tbody>
</table>

→ No obvious difference in material structure.
Growth of different CNW in CH4/H2
Growth of CNW in CH4/H2 and radicals

(a) Growth rate as a function of total pressure

(b) Growth rate as a function of VHF power

(a) Density of CNWs

(b) Density of radicals

(c) Density of radicals
Where do we stand?

1) The **CNWs density is controlled by the total pressure**, and very-high-frequency CHF power as well as surface temperature.
2) No change in the crystal quality (Raman) and the chemical bonding states (XPS) is observed between CNWs.
3) **H-atom density was linearly correlated with the wall density**.
4) RI-PECVD of CNWs the relative composition in CH and H atom is at least indicator of film quality control.
5) We think that **F atoms** from C2F6/H2 plasma might **act as a dopant** at the graphene edges. Consequently, electrical properties could be controlled while maintaining the crystal quality and chemical bonding state.
Role of substrate and effect of catalyst

Substrate materials
- Transition metal substrates
- Dielectric substrates
- Cylindrical substrates

Process
- Surface defects
- Dangling bonds between carbon radicles and substrate defects
- Nucleation and Formation of nanoislands
- Formation of graphitic layer
- Growth of CNWs
- Plasma-surface interaction
Conclusions

Growth and processing of vertically aligned 2D carbon nanowalls, and studying the characteristic features for future applications

- PECVD Hydrocarbon/Fluorocarbon sources
- Plasma treatment on carbon hydrogels
- Finding optimum discharge parameters and Growth of CNWS
- Functionalization
  - Vertical growth
  - Surface morphology
  - Enhance electronic properties
  - Band gap tuning
  - Finding applications

Growth and processing of vertically aligned 2D carbon nanowalls, and studying the characteristic features for future applications