A New Generation of Nanotechnological Product and Process

Large-Area Synthesis of High-Quality and Controllable Thickness Graphene Films by Rapid Thermal Annealing

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Rapid Thermal Annealing (RTA)

- Nickel–assisted graphene growth using RTA

- Spontaneous formation, Carbon- and oxygen-containing compounds
- Few-layer graphene films were formed on a nickel surface
Rapid Thermal Annealing (RTA)
- Temperature (800 ~ 1000°C) & Various ambient

- Few-layer graphene films are formed under vacuum (∼10⁻³ Torr) at temp. ranging from 800 °C and 1000 °C for 0.5 – 4min
- No graphene form when inert gases are introduced during the RTA process
GROWTH MECHANISM

- Dominant factor – oxygen evaporation rate

1) Inert gas - RTA
   No significant change in oxygen concentration
   → No graphene form

2) Vacuum – RTA
   Graphene forms in all investigated temperature, along with oxygen evaporation from surface

- Presence of Ar or N₂ during RTA may lead to a much reduced oxygen evaporation rate
  → The oxygen atoms desorbing from the surface have a finite probability of being reflected back to the nickel surface by collision with Ar or N₂, as pointed out by Langmuir and Fonda. (Phys. Rev. 43, 401 (1912), (Phys. Rev. 31 (260))
Characterization of graphene at RTA-vacuum

The thickness and physical properties of the graphene layers are strongly dependent on the RTA temperature and time.
CONCLUSION

- The *merits* of our method are as follows.

  1) Simply grown by annealing the nickel films at high temperature under vacuum
  2) The consuming time of process is highly short
  3) The thickness of graphene layers is controlled by RTA temperature and time
  4) Comparable structural and optoelectronic qualities with CVD-graphene
THANK YOU
Facile Synthesis of Few-Layer Graphene with a Controllable Thickness Using Rapid Thermal Annealing

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ABSTRACT: Few-layer graphene films with a controllable thickness were grown on a nickel surface by rapid thermal annealing (RTA) under vacuum. The instability of nickel films in air facilitates the spontaneous formation of ultrathin (<2–3 nm) carbon- and oxygen-containing compounds on a nickel surface; thus, the high-temperature annealing of the nickel samples without the introduction of intentional carbon-containing precursors results in the formation of graphene films. From annealing temperature and ambient studies during RTA, it was found that the evaporation of oxygen atoms from the surface is the dominant factor affecting the formation of graphene films. The thickness of the graphene layers is strongly dependent on the RTA temperature and time, and the resulting films have a limited thickness (<2 nm), even for an extended RTA time. The transferred films have a low sheet resistance of ~0.9 ± 0.4 kΩ/sq, with ~94% ± 2% optical transparency, making them useful for applications as flexible transparent conductors.

KEYWORDS: graphene, rapid thermal annealing (RTA), few-layer, nickel, crystallization, transparent conductor
Supporting Information
Experiments (RTA method)

• The nickel films
  - Deposited in commercial evaporators (~$10^{-6}$-$10^{-7}$ Torr) with solid Ni(99.99%)
  - Thickness of ~ 100nm deposited on a SiO$_2$(300nm)/Si(100) substrate
  - The source and stored under atmosphere for a typical period of a few days.

• RTA (Rapid Thermal Annealing)
  - Temperatures ranging from 800 °C to 1,000 °C for 0.5 - 4 min
  - Vacuum ($\sim 10^{-3}$ Torr)
  - In inert gas (Ar, N$_2$) ambient ($\sim 0.2$-2.0 Torr)

• How to employ the source of carbon
  - Trace amounts of unintentionally introduced carbon and oxygen atoms after Ni deposition
## How to make graphene?

**Table 1. Comparison of different methods for graphene production**

<table>
<thead>
<tr>
<th>Schematic</th>
<th>Methods</th>
<th>Pros. &amp; Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Schematic" /></td>
<td><strong>Top Down</strong>&lt;br&gt;Mechanical Exfoliation (scotch Tape)</td>
<td>• High quality graphene&lt;br&gt;• only Lab. Scale</td>
</tr>
<tr>
<td><img src="image2.png" alt="Schematic" /></td>
<td>Chemical Exfoliation&lt;br&gt;(Graphite $\rightarrow$ Go $\rightarrow$ RGO)&lt;br&gt;(Graphite $\rightarrow$ Graphene)</td>
<td>• Good dispersion in various solvent&lt;br&gt;• Large Area processing&lt;br&gt;• Good adhesion for composite&lt;br&gt;• High Defect Density</td>
</tr>
<tr>
<td><img src="image3.png" alt="Schematic" /></td>
<td><strong>Bottom Up</strong>&lt;br&gt;CVD (Chemical Vapor Deposition)</td>
<td>• Excellent electrical properties&lt;br&gt;• Large area processing&lt;br&gt;• Additional steps for composite</td>
</tr>
<tr>
<td><img src="image4.png" alt="Schematic" /></td>
<td>Epitaxial Growth&lt;br&gt;(SiC wafer)</td>
<td>• High quality graphene&lt;br&gt;• only Lab. scale</td>
</tr>
</tbody>
</table>
Rapid Thermal Annealing (RTA)

- An attractive method
- Large area graphene synthesis > 6 inch
- Good optical, electrical, and mechanical properties
- Applying various applications

Why should the CVD method be improved?
1) Required various parameters
2) Difficult control for growth.
3) Total process time is long.
4) Price.

RTA method
- Facile synthesis of large-area graphene
- A simple and reproducible method
- Without intentional carbon-containing precursor

How to employ the source of carbon
- XPS concentration-depth profile of Ni films before RTA process

- The presence of Ultrathin Compounds on a Nickel Surface

<table>
<thead>
<tr>
<th></th>
<th>C 1s</th>
<th>O 1s</th>
<th>Ni 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni3C</td>
<td>283.9 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiCO3</td>
<td>288.4 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiO</td>
<td>529.7 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiCO3</td>
<td>531.3 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni3C</td>
<td>852.9 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiO</td>
<td>853.8 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiCO3</td>
<td>854.7 eV</td>
<td></td>
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</tr>
</tbody>
</table>

Trace amounts of unintentionally introduced carbon and oxygen atoms after Ni deposition
What makes difference growth condition?
- XPS concentration profile

1) As deposition, 2) RTA in N2 at 900°C 1min, 3) RTA in vacuum at 900°C 1min

- considerable compositional changes only vacuum ambient
- most oxygen atoms disappear after the vacuum – RTA process
What makes difference growth condition?
- XPS Depth profile

- 1) As deposition, 2) RTA in N2 at 900°C 1min, 3) RTA in vacuum at 900°C 1min

Table 4. the composition(%) of the top surface according to C1s and O1s

<table>
<thead>
<tr>
<th>Ambient</th>
<th>Carbon composition(%)</th>
<th>Oxygen composition(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-grown</td>
<td>27.73%</td>
<td>35.68%</td>
</tr>
<tr>
<td>RTA in N2</td>
<td>25.26%</td>
<td>30.94%</td>
</tr>
<tr>
<td>RTA in vacuum</td>
<td>85.92%</td>
<td>2.36%</td>
</tr>
</tbody>
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