CVD growth of Graphene

SPE ACCE presentation

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James M. Tour group

September 9 to 11, 2014
Graphene

History

1500: Pencil-Is it made of “lead”?  
1789: Graphite  
1987: The first use of the term “graphene”  
2004: Single-layer graphene discovered  
2009: Large-area CVD graphene on Cu  
2010: Nobel Prize in physics  
Today ……
What is Graphene?

- Thinnest material (one-atom thick)
- Impermeable to gases and ions
- High intrinsic mobility ($\mu \geq 200,000 \text{ cm}^2/\text{Vs}$)
- Large surface area (> 2630 m$^2$/g)
- Highly transparent (~ 2.3% absorption for visible light)
- Record thermal conductivity (5300 W/m·K, outperforming diamond)
- Strongest material ever measured (>100 times than steel)
- Stiffest known material (stiffer than diamond)
- Most stretchable crystal (up to 20% elastically)
- Highest current density at room T
- ......
High-Speed Transistors

Nature 467, 305 (2010)

Touch Screen: Flexible!


Graphene Liquid Cell

Science 336, 61 (2012)

Energy Storage

Nano. Lett. 8, 3498 (2008)

DNA Sequencing

Nature 467, 190 (2010)

H₂ Storage

Nano. Lett. 8, 3166 (2008)
Graphene-based Heterostructures

planar graphene/h-BN

vertical graphene/h-BN

vertical graphene/CNTs


*Nat. Mater.* 12, 792 (2013)

*Nano. Lett.* 11, 2032 (2011)

Preparation of Graphene

- Mechanical exfoliation: excellent quality but small size

- Chemical exfoliation: large-scale method but low quality

- Chemical vapor deposition (CVD): good quality and large size; & The topic here
➢ Exfoliated graphene is limited to micron sizes

➢ CVD graphene could be grown up to 30 inches

CVD Synthesis of Graphene Based-Materials

1. Growth of Graphene from Solid Carbon Sources
2. Synthesis of Bilayer Graphene on Insulating Substrates
3. Growth of Graphene Single Crystals
4. Graphene and Carbon Nanotube Hybrid Materials
CVD System for Graphene Growth
Graphene from Solid Carbon Source

$\text{PMMA/Cu/SiO}_2/\text{Si} \xrightarrow{\text{H}_2/\text{Ar}, 10 \text{ min}} \text{Graphene/Cu/SiO}_2/\text{Si}$

Counts (a.u.) vs. Raman shift (cm$^{-1}$):
- Few-layer
- Bilayer
- Monolayer

Absorption vs. Wavelength (nm):
- 268 nm, $T = 94.3\%$
- Monolayer $T = 97.1\%$

Graphene from Girl Scout Cookies
SEM of the Cu foil after growth of graphene from a Girl Scout cookie. (A) The original frontside of the Cu; (B) The backside of the Cu foil
Graphene Derived from Cookies

• The online price for a 2 inch by 2 inch CVD graphene is 250 dollars.
• One box of girl scouts cookies weighs 255 g and can be made into 157,800 m² graphene, which can cover 29.5 American football fields.
• The price for that large of graphene will worth 15,290,697,674 dollars.

http://www.youtube.com/watch?v=IoLvULmacw4

Commercial source of graphene
https://graphene-supermarket.com/CVD-grown-graphene/
Graphene Derived from a Different Carbon Source

Ar: 500 cm$^3$ STP min$^{-1}$
H$_2$: 100 cm$^3$ STP min$^{-1}$

Cross view of the growth of graphene on the backside of the Cu foil

(Cockroach leg)

(Graphene)
Graphene on Different Substrates

- Graphene on Glass
- Graphene on Polymer
Figure. Diffraction pattern and TEM images of the cookie-derived graphene. (A) SAED pattern, (B) suspended graphene film on a 1 µm diameter hole and (C) the edge of monolayer graphene.

Done by Sun, Z
XPS of Graphene

A. Girl Scout cookie-derived graphene

B. Chocolate-derived graphene

C. Grass-derived graphene

D. Plastic-derived graphene

E. Dog feces-derived graphene

F. Roach-derived graphene
UV-Vis of Graphene

A. Girl Scout cookie-derived graphene

B. Chocolate-derived graphene

C. Grass-derived graphene

D. Plastic-derived graphene

E. Dog feces-derived graphene

F. Roach-derived graphene
Raman Spectra of Graphene

A. Cookie-derived graphene
B. Chocolate-derived graphene
C. Grass-derived graphene
D. Plastics-derived graphene
E. Dog waste-derived graphene
F. Roach-derived graphene
Thickness Control

The 2D peak, $\sim 2700$ cm$^{-1}$ dominates the monolayer graphene
The G peak $\sim 1600$ cm$^{-1}$ dominates multi-layer graphene
The D peak $\sim 1350$ cm$^{-1}$ indicates defects and functionalization
1.2 N-Doped Graphene Made from Solid Carbon Sources

(a) Pristine graphene

(b) N-doped graphene

(c) Pristine

(d) N-doped
C diffused through nickel form graphene on SiO$_2$

Graphene grows under the nickel layer

Z. Peng*, Z. Yan* et al. ACS Nano 5, 8241 (2011)
Growth Mechanism

The carbon is expelled as solubility decreases upon cooling.
Polycrystalline CVD graphene

Nature 469, 389 (2011)
Synthesis of Wafer-Scale Single-Crystal Graphene

CVD graphene is polycrystalline

Two main methods to reduce graphene seed density:

- Electrochemical polishing
- High-pressure annealing

Cu surface pretreatments

ACS Nano 6, 9110 (2012)
Electrochemical Polishing – removes surface impurities

Heating in air at 200°C for 1 min
High-Pressure Annealing – flattens the surface

Annealing typically in 2 atm absolute pressure of hydrogen for several hours
Millimeter-Sized Monolayer Graphene domains grown on Pretreated Cu

Electron diffraction pattern the same for several sites
Graphene Domains Transferred on SiO$_2$/Si Wafers
Synthesis of Wafer-Scale Single-Crystal Graphene

The carrier mobility is as high as 11,000 cm²/V s on SiO₂/Si substrates at room temperature, comparable to that of exfoliated graphene.
Graphene Domains across Grain Boundaries of Cu

Grain boundaries in the copper do not interfere with growth of the single domain
3.2 Bi- and Tri-layer Graphene Single Crystals (graphene pyramids)

0-0 Bilayer graphene domains are Bernal-stacked
Hexagonal Onion-Ring-like Graphene Domains

Electronic Characterizations

Graph a: Plot of $\rho$ ($\Omega/\square$) vs. $n \times 10^{12}$ cm$^{-2}$

Graph b: Plot of $\mu_{FE}$ (cm$^2$/V s) vs. $n \times 10^{12}$ cm$^{-2}$

With Javen
Growth Mechanism

- Panel a: Cu foil with monolayer graphene and C adatoms.
- Panel b: Edge nucleation to form a graphene ribbon.
- Panel c: New edge exposure.
- Panel d: Repeated edge nucleation.
- Panel e: Repeated growth to form a hexagonal structure.

The diagram illustrates the process of graphene growth on a Cu foil through edge nucleation and repeated growth.
Growth of Bi, Tri, and Tetralayer Graphene

Pristine Cu foil → \( \text{H}_2 \) at 1000 °C → Annealed Cu foil → \( \text{H}_2, \text{CH}_4 \) at 1000 °C → Graphene on Cu foil

Removed some impurities on Cu surface

Graphene Layers vs. \( \text{CH}_4 \) Partial Pressure (Torr)

- 1L
- 2L
- 3L
- 4L

\( \frac{P_{\text{H}_2}}{P_{\text{CH}_4}} \approx 28 \)
Bernal Graphene 2D Band Fitted with Lorentzians

Bilayer graphene fits 4 Lorentzians
Trilayer graphene fits 6 Lorentzians
Tetralayer graphene fits 3 Lorentzians
Visible Spectra of Bi, Tri, and Tetralayer Graphene

Transmittance at 550 nm

- 95.4% (2 L)
- 93.0% (3 L)
- 90.4% (4 L)

Wavelength (nm)

Transmittance (%)
Electron Diffraction and TEM Images of Bi, Tri, and Tetralayer Graphene

Bi: \( \frac{I_{1-210}}{I_{1-100}} \) is \( \sim 3.5 \)

Tri: \( \frac{I_{1-210}}{I_{1-100}} \) is \( \sim 4.5 \)

Tetra: \( \frac{I_{1-210}}{I_{1-100}} \) is \( \sim 6.3 \)
Graphene-Dominated Electronic Properties

Graphene - Dominated Electronic Properties

With Javen

(a) Resistivity ($\Omega$) vs. $n$ ($\times 10^{12}$ cm$^{-2}$)

(b) $\mu FE$ (cm$^2$V$^{-1}$s$^{-1}$) vs. $n$ ($\times 10^{12}$ cm$^{-2}$)
Rebar Graphene-Based Flexible Transparent Electrodes

(a) Sheet Resistance: ~ 600 $\Omega/\square$
T = 95.8 % at 550 nm

Pluronic 127 wrapped NTL CNTs

(b) NTL CNTs

30 nm
10 nm

(c)
4.2 Metal-Graphene-Carbon Nanotube Multifunctional Hybrids

Z. Yan*, L. Ma* et al. ACS Nano 7, 58 (2013)
TEM, Raman Characterizations and Length Control Growth on porous nickel foam
Turn-on field is around 0.27 V/µm, one of the smallest value ever reported.
Fuctionalization of Graphene

• Non-covalent functionalization: $\pi-\pi$ interaction, polymer coating

• Covalent functionalization: Hydrogenation, fluorination, intercalation, oxidation, diazonium chemistry, etc.
## XPS of F-Graphene

<table>
<thead>
<tr>
<th>Temperature</th>
<th>C%</th>
<th>F%</th>
<th>C : F</th>
</tr>
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<tbody>
<tr>
<td>25°C, 15min</td>
<td>89.7</td>
<td>10.3</td>
<td>8.7:1</td>
</tr>
<tr>
<td>50°C, 15min</td>
<td>83.5</td>
<td>16.5</td>
<td>5.1:1</td>
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<tr>
<td>100°C, 15min</td>
<td>79.8</td>
<td>20.0</td>
<td>4.0:1</td>
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<tr>
<td>150°C, 15min</td>
<td>74.7</td>
<td>25.3</td>
<td>3.0:1</td>
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<td>200°C, 15min</td>
<td>71.0</td>
<td>29.0</td>
<td>2.4:1</td>
</tr>
</tbody>
</table>

The C : F ratio can be tuned by changing the temperature of fluorination.
Raman Spectra of F-Graphene
Modulation of Graphene Electronic Properties

Graphs showing the modulation of current ($I_d$) vs. gate voltage ($V_g$) for NH$_2$-SAMs and F-SAMs.
Additional Work

Graphene Supperlattice

Graphene-CNT Bonds

Transparent Memory

*Nat. Commun.* 2, 559 (2011)


Microsupercapcitor

Terahertz Spectroscopy

Graphene Fibers

*Nano. Lett.* 13, 72 (2013)

*Nano. Lett.* 12, 3711 (2012)

Graphene/Metal Grids for Transparent Electrodes

Graphene nanoribbon/SnO_2 for Lithium Batteries

Graphene nanoribbon for Gas Barriers

Thermal Conduction of h-BN

Graphene Functionalization

Graphene/Metal Grids for Solar Cells

CVD Graphene Thickness Control

Coal-Derived Graphene Quantum Dots
V. Conclusion

- Both pristine and N-doped graphene could be made from solid carbon sources;
- Bilayer graphene could be directly grown on insulating substrates;
- Millimeter-sized monolayer graphene single crystals could be grown on polycrystalline Cu;
- Graphene domains with special spatial structures, such as hexagonal graphene onions and graphene pyramids, could be synthesized by CVD method on Cu;
- Planar and vertical graphene/CNTs hybrid materials can be fabricated for multifunctional applications;
- Electronic properties of graphene could be modulated by chemical methods and atom substitution.

James M. Tour Research Group

Collaborators:
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Dr. Pulickel Ajayan
Dr. Angel Marti
Dr. Zhengzong Sun

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Thank You!

Questions