Graphene sensors – detection of gases

Chapters of Nanostructures
TU Liberec

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Allotropes of carbon

[Diagram showing various allotropes of carbon including Diamond, Amorphous, Fullerene (60), SWCNT, Graphite, and Graphene, along with sp3 and sp2 bonding representations.]
Allotropes of carbon

Graphene

- Allotrope of carbon
- Single layer of atoms
- Two-dimensional hexagonal lattice
- Indefinitely large aromatic molecule
- Ultimate case of polycyclic aromatic hydrocarbons
- $sp^2$
Unique properties of graphene

2 630 m²·g⁻¹
0,76 mg·m⁻²
1,1 TPa
5 000 W·m⁻¹·K⁻¹
2,3% absorption
10⁸ S·m⁻¹
4 510 K
1,6·10⁹ A·cm⁻²

nanosilica 1 200 m²·g⁻¹

Unique properties of graphene

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0,76 $\text{mg}\cdot\text{m}^{-2}$
1,1 TPa
5 000 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
2,3% absorption
$10^8$ $\text{S}\cdot\text{m}^{-1}$
4 510 K
$1,6\cdot10^9$ $\text{A}\cdot\text{cm}^{-2}$

KRISHNAN, Siva Kumar, 2019. RSC Advances.
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steel 0,2 TPa
diamond 1 000 – 2 300

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**4 510 K**
1,6·10$^{9}$ A·cm$^{-2}$
nanosilica 1 200 m$^{2}$·g$^{-1}$
steel 0,2 TPa
diamond 1 000 – 2 300
silver 6,3·10$^{7}$ S·m$^{-1}$
tungsten 3 695 K
Unique properties of graphene

- Surface area: 2630 m²·g⁻¹
- Density: 0.76 mg·m⁻²
- Elastic modulus: 1.1 TPa
- Thermal conductivity: 5000 W·m⁻¹·K⁻¹
- Absorption: 2.3%
- Electrical conductivity: 10⁸ S·m⁻¹
- Melting point: 4510 K
- Electrical current density: 1.6·10⁹ A·cm⁻²

Comparison with other materials:
- Nanosilica: 1200 m²·g⁻¹
- Steel: 0.2 TPa
- Diamond: 1,000 – 2,300
- Silver: 6.3·10⁷ S·m⁻¹
- Tungsten: 3,695 K
- Copper: 10⁵ A·cm⁻²
Preparation of graphene

_Hummer’s method_

graphite powder washed in aqua regia, heating, water treatment, drying $\rightarrow$ $9 \text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4 \rightarrow$ slow addition of $\text{KMnO}_4$, stirring 6 h $\rightarrow \text{H}_2\text{O}_2$, cooling $\rightarrow$ washed with $\text{HCl} + \text{DI water}$ three times $\rightarrow$ intense heat $\rightarrow$ sonification $\rightarrow$ heating $\rightarrow \text{NaHSO}_3 + \text{Na}_2 \cdot 9\text{H}_2\text{O} + \text{SO}_2$, stirring $\rightarrow$ filtration, DI water $\rightarrow$ freeze drying

Preparation of graphene

Mechanical exfoliation

- adhesive tape stucked over graphite crystals or flakes leads to entrapment of graphite layers
- multiple steps, each produces fewer layer
- deposition on silicon wafer
- crystallites larger than 1 mm, visible

Preparation of graphene

*CVD*

- quartz furnace with inert environment is heated
- carbonaceous gases $\text{Ar}/\text{H}_2/\text{CH}_4$
- deposition of carbon on the metal ($\text{Ni}/\text{Cu}/\text{Co}/\text{Pt}/\text{Ir}$)
- formation of single long atom-thick mono-layer of graphene

Application of graphene

EVERYWHERE

- **Medicine** (contrast agent, drug delivery, ...)
- **Electronics** (transistors, quantum dots, conductive inks, organic electronics, transparent electrodes, ...)
- **Energy** (solar cells, storage)
- **Environmental** (pollution removal, water filtration, ...)
- **Composites**
Graphene-based sensors

*Types of sensors*

- Electrochemical
- Strain
- Electrical

Graphene-based gas sensors

Gas sensors

- electronic device that can qualitatively or quantificationally detect specific gases
- conventionally constructed by semiconductor metal oxides
  - drawbacks: high-temperature operation, large power consumption, low selectivity or conducting polymers
  - degradation

Graphene-based gas sensors

Why?

- All atoms are exposed to surface interactions with gas molecules
- Room temperature, strong and flexible
- Easy functionalization is able to improve sensing performance
Graphene-based gas sensors

Mechanism

- gaseous adsorbates interact with graphene
- charge transfer processes between gas molecules and graphene surface
  - redistribution of electrons (H₂O)
  - change in electron concentration (NO₂)
  - covalent bonding (H·, HO·)
- leads to conductance changes

Graphene-based gas sensors

Types

- Chemiresistors – simply, sensitive, stable
  - sensing layer between electrodes
  - resistance/current monitoring
- FET (field effect transistor)
  - source, drain, gate
  - observing output characteristics
Graphene-based gas sensors

- Changes in resistivity
- (II) 5 L of diluted gas
  1 ppm
- (III) evacuation
- (IV) annealing at 150 °C

Graphene-based gas sensors

- Changes in resistivity
- Variable temperatures
- 5 ppm of NO₂

Graphene-based gas sensors

Defective Graphene / Pristine Graphene hybrid layer

Graphene-based gas sensors

<table>
<thead>
<tr>
<th>Material</th>
<th>Device type</th>
<th>Synthesis method</th>
<th>Substrate</th>
<th>Analyte</th>
<th>Limit of detection</th>
<th>Working temperature</th>
<th>Response (recovery) time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene + MoS₂</td>
<td>Resistive</td>
<td>CVD + mechanical exfoliation</td>
<td>Polyimide</td>
<td>NO₂</td>
<td>1.2 ppm</td>
<td>150 °C</td>
<td>30 min</td>
</tr>
<tr>
<td>Graphene + MoS₂</td>
<td>Resistive</td>
<td>Liquid-phase co-exfoliation</td>
<td>Si/SiO₂</td>
<td>Methanol</td>
<td>10 ppm</td>
<td>–</td>
<td>210 s (220 s)</td>
</tr>
<tr>
<td>Graphene + MoS₂</td>
<td>Resistive</td>
<td>GA + ATM</td>
<td>Poly-Si</td>
<td>NO₂</td>
<td>50 ppb</td>
<td>25 °C</td>
<td>21.6 s (&lt; 29.4 s)</td>
</tr>
<tr>
<td>Graphene + MoS₂</td>
<td>FET</td>
<td>CVD + mechanical exfoliation</td>
<td>Si/SiO₂</td>
<td>NO₂</td>
<td>1 ppm</td>
<td>RT</td>
<td>–</td>
</tr>
<tr>
<td>rGO + MoS₂</td>
<td>Resistive</td>
<td>Microwave-assisted exfoliation</td>
<td>PDMS</td>
<td>NH₃</td>
<td>0.48 mbar</td>
<td>RT</td>
<td>15 s</td>
</tr>
<tr>
<td>rGO + MoS₂</td>
<td>Resistive</td>
<td>Soft lithographic patterning</td>
<td>PET</td>
<td>NO₂</td>
<td>0.15 ppm</td>
<td>90 °C</td>
<td>–</td>
</tr>
<tr>
<td>rGO + MoS₂</td>
<td>Resistive</td>
<td>Lithography</td>
<td>SiO₂/Si</td>
<td>NO₂</td>
<td>2 ppm</td>
<td>60 °C</td>
<td>30 min</td>
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<tr>
<td>rGO + MoS₂</td>
<td>Resistive</td>
<td>Layer-by-layer self-assembly</td>
<td>SiO₂/Si</td>
<td>Formaldehyde</td>
<td>2.5 ppm</td>
<td>RT</td>
<td>73 s</td>
</tr>
<tr>
<td>rGO + MoS₂</td>
<td>Resistive</td>
<td>Self-assembly</td>
<td>PEN</td>
<td>Formaldehyde</td>
<td>2.5 ppm</td>
<td>RT</td>
<td>10 min (13 min)</td>
</tr>
<tr>
<td>MoS₂/WS₂</td>
<td>Resistive</td>
<td>Hydrothermal process</td>
<td>–</td>
<td>NO₂</td>
<td>10 ppb</td>
<td>RT</td>
<td>1.6 s (27.7 s)</td>
</tr>
<tr>
<td>rGO/WS₂</td>
<td>Resistive</td>
<td>Ball milling and sonication</td>
<td>Si₃N₄</td>
<td>NO₂</td>
<td>1 ppm</td>
<td>RT</td>
<td>22 min (26 min)</td>
</tr>
<tr>
<td>Defective graphene/pristine graphene</td>
<td>Current</td>
<td>APCVD</td>
<td>Ge</td>
<td>NO₂</td>
<td>1 ppm</td>
<td>RT</td>
<td>28 s (238 s)</td>
</tr>
<tr>
<td>rGO-MoS₂-CdS</td>
<td>Resistive</td>
<td>Solvothermal Mechanically exfoliated + e-beam lithography</td>
<td>–</td>
<td>NO₂</td>
<td>0.2 ppm</td>
<td>75 °C</td>
<td>25 s (34 s)</td>
</tr>
<tr>
<td>BP/h-BN/MoS₂</td>
<td>FET</td>
<td></td>
<td>SiO₂/Si</td>
<td>NO₂</td>
<td>3.3 ppb</td>
<td>RT</td>
<td>8 min (8 min)</td>
</tr>
</tbody>
</table>

Graphene-based gas sensors

- Graphene + MoS$_2$
  (conductive layer + analyte acceptor)

Graphene-based gas sensors

- Graphene + MoS$_2$
  (conductive layer + analyte acceptor)

Graphene-based gas sensors

- Graphene + MoS$_2$ (conductive layer + analyte acceptor)
- Polyimide substrate
- 5,000 bending cycles

Summary

- Sensitivity: 1 ppm, special cases 1 ppb
- Selectivity: DGr/Gr
- Response/recovery time: 65x higher response for NO₂
- Material stability: tens/
- Reproducibility hundreds of seconds
- temperature, humidity
Summary

- Sensitivity: 1 ppm, special cases 1 ppb
- Selectivity: DGr/Gr
- Response/recovery time: 65x higher response for NO₂
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hundreds of seconds
- Material stability: temperature, humidity
- Reproducibility

Thank you for your attention.
References


