2D Materials: Properties, Applications and Synthesis Methods

Joan Redwing
4/14/2016
Where is Penn State?
Penn State Information

- Land grant institution, founded in 1855
- Located in State College, Pennsylvania (population~100,000)
- Enrollment ~45,000 students
Materials Research at Penn State

• 200+ faculty, 800+ grad students, 15 academic departments
• Materials Research Institute
• Millennium Science Complex
  • Huck Institute for Life Sciences and Materials Research Institute
  • Nanofabrication Facility (part of National Nanofabrication Infrastructure Network)
  • Materials Characterization Facility
Electronic Materials Synthesis

Our research is focused on the development of new processes, materials and device structures using chemical vapor deposition-based techniques.

Thin Films

Nanoscale Materials

Process Chemistry ↔ Material Structure ↔ Properties ↔ Device Applications
$17.8M national user facility to advance synthesis of 2D materials for next generation electronics

2D chalcogenide monolayers, surfaces and interfaces are emerging as a compelling class of systems with transformative new science that can be harnessed for novel device technologies in next-generation electronics.

An NSF user facility with broad access:

- Open calls for user proposals,
- No user fees for academic use
- Access to a team of local experts
- Community knowledge-base of synthetic protocols

- Webinars, Workshops, Website resources
- Partnership opportunities with PUI, MSI

mip.psu.edu
Graphene

- Single layer of carbon atoms

Properties:
- Mechanically strong
- Flexible
- Optically transparent
- Good conductor of heat and current
- Semi-metal
- Graphene nanoribbons are semiconducting
Applications for Graphene

- High speed Transistor
  RFIC, Sensor

- Conductive ink
  EMI screen ink

- Flexible Display
  Touch Panel

- Semiconductor

- Ink & paste

- Chemical sensors

- Solar cell, Battery
  Supercapacitor

- TCO

- Barrier

- Energy

- Heat spreader

- Composites

- LED lighting

- Automobile
  Air plane components
Beyond Graphene....


2D Chalcogenides

- Graphene-like layered materials
- Exhibit wide variety of electronic properties – insulators, semiconductors, metals, superconductors

Q.H. Huang, et al.

A.K. Geim and I.V. Grigorieva

<table>
<thead>
<tr>
<th>Graphene family</th>
<th>Graphene</th>
<th>hBN ‘white graphene’</th>
<th>BCN</th>
<th>Fluorographene</th>
<th>Graphene oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D chalcogenides</td>
<td>MoS$_2$, WS$_2$, MoSe$_2$, WSe$_2$</td>
<td></td>
<td></td>
<td></td>
<td>Metallic dichalcogenides: NbSe$_2$, NbS$_2$, TaS$_2$, TiS$_2$, NiSe$_2$ and so on</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Layered semiconductors: GaSe, GaTe, InSe, Bi$_2$Se$_3$ and so on</td>
</tr>
</tbody>
</table>

A.K. Geim and I.V. Grigorieva
Thickness-Dependent Properties

- Dramatic changes in optical and electronic properties as material is thinned from bulk to a monolayer (1 layer)
  - In-direct bandgap to direct bandgap semiconductor
  - Changes in symmetry – alters polarization

Y.F. Chen, et al.
Van der Waals bonding enables stacking of different materials without need to form chemical bonds.
2D Electronics

- Transistors made of atomically thin layers (good for electrostatics)
- Transfer of 2D layers onto plastic substrates for flexible electronics

Q.H. Huang, et al.
The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets

Manish Chhowalla*1, Hyeon Suk Shin2, Goki Eda3,4,5, Lain-Jong Li6, Kian Ping Loh4,5 and Hua Zhang7
Most Common Structures of TMDs

2H configuration

- semiconductor
- Trigonal prismatic (2H)

1T configuration

- semimetal
- Octahedral (1T)

Electronic character of 2D chalcogenides

<table>
<thead>
<tr>
<th>Group</th>
<th>M</th>
<th>X</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Ti, Hf, Zr</td>
<td>S, Se, Te</td>
<td>Semiconducting ((E_g = 0.2-2 \text{ eV})). Diamagnetic.</td>
</tr>
<tr>
<td>5</td>
<td>V, Nb, Ta</td>
<td>S, Se, Te</td>
<td>Narrow band metals ((\rho \sim 10^{-4} \text{ \Omega cm})) or semimetals. Superconducting. Charge density wave (CDW). Paramagnetic, antiferromagnetic, or diamagnetic.</td>
</tr>
<tr>
<td>6</td>
<td>Mo, W</td>
<td>S, Se, Te</td>
<td>Sulfides and selenides are semiconducting ((E_g \sim 1 \text{ eV})). Tellurides are semimetallic ((\rho \sim 10^{-3} \text{ \Omega cm})). Diamagnetic.</td>
</tr>
<tr>
<td>7</td>
<td>Tc, Re</td>
<td>S, Se, Te</td>
<td>Small-gap semiconductors. Diamagnetic.</td>
</tr>
<tr>
<td>10</td>
<td>Pd, Pt</td>
<td>S, Se, Te</td>
<td>Sulfides and selenides are semiconducting ((E_g = 0.4 \text{ eV})) and diamagnetic. Tellurides are metallic and paramagnetic. PdTe(_2) is superconducting.</td>
</tr>
</tbody>
</table>

\(\rho\) in-plane electrical resistivity.
Band alignment of layered chalcogenides
From Monolayer to Bulk: Photoluminescence Change

Photoluminescence spectra

Energy band structure

- With increasing number of layers, the photoluminescence intensity decreases, due to energy band changes.
- Monolayer MoS$_2$: direct bandgap.
- Bilayer or thicker MoS$_2$: indirect bandgap.
- This suggests strong interlayer interaction.
Bulk 2D chalcogenides (MoS$_2$ example)

- Naturally occurring in molybdenite ore
  - Powder used in lubricants

- Bulk synthesis methods (for higher purity material):
  - Sulfurization of MoO$_3$ powder (Heat in H$_2$S, etc.)
  - Chemical vapor transport

Manchester Nanocrystals
Chemical exfoliation of TMDs (MX$_2$)

Mechanism of exfoliation

Li-intercalation

2H-MX$_2$

BuLi

Hexane

1T-MX$_2$

Exfoliation

H$_2$O

sonication


M. Chhowalla, et al.
Metal transformation

"Soft Chalcogenization"

$$M_{(s)} + X_{2(g)} \rightarrow MX_{2}$$

Solid State Reactions

$$M_{(s)} + X_{2(s)} \rightarrow MX_{2}$$
Powder vapor transport
(also referred to as chemical vapor deposition)

M. Chhowalla, et al.
Powder vapor transport

Powder Vaporization

The Case of MoS$_2$

- Non-uniform vaporization of MoO$_3$

Courtesy: Kyma Technologies
Powder Vapor Transport


Nature Nanotechnology 9, 1024–1030 (2014)

Powder Vaporization

Chem. Mater., 2014, 26 (22), pp 6371-6379
Point defects

Figure 1 | Atomic resolved STEM-ADF images to reveal the distribution of different point defects. (a) Antisite defects in PVD MoS$_2$ monolayers. Scale bar, 1 nm. (b) Vacancies including $V_S$ and $V_{S2}$ observed in ME monolayers, similar to that observed for CVD sample. Scale bar, 1 nm. (c,d) Histograms of various point defects in PVD, CVD and ME monolayers. Error estimates are given for the dominant defects (more details on the statistics can be found in Supplementary Fig. 6). ME data are in green, PVD data in red and CVD in blue.
Chemical Vapor Deposition

Advantages:
- Scalable to large substrate diameters
- Offers good control over deposition rate
- Can easily change precursors for growth of heterostructures

Variety of precursors:
- Mo(CO)$_6$, MoCl$_5$
- W(CO)$_6$, WF$_6$
- H$_2$Se, (CH$_3$)$_2$Se, SeCl$_4$
- H$_2$S, (C$_2$H$_5$)$_2$S

Challenges:
- Mo, W, etc. high melting points (>2000°C)/low vapor pressure
- S, Se, etc. low melting points (<250°C)/high vapor pressure
MOCVD of WSe$_2$

- Very low flow rates of W(CO)$_6$ required for monolayer growth
- High Pressure (650 Torr)
- 100% Hydrogen ambient
- Raman and PL indicative of monolayer growth

High flow rates of MO precursors leads to thick WSe$_2$ films, and significant vertical growth

Collaboration with Josh Robinson (PSU MatSE)
MOCVD of WSe$_2$

c-plane (0001) sapphire

Growth Conditions:
- W(CO)$_6$, (CH$_3$)$_2$Se, H$_2$ carrier gas
- 800°C, 700 Torr
- W(CO)$_6$=3.3x10$^{-4}$ sccm, Se/W=2.4x10$^5$

Normalized Raman Mapping

Normalized PL Mapping

Raman Mapping

PL Mapping 1.60 eV
MOCVD of WSe$_2$: Effect of Se/W Ratio

- Defects serve as nucleation sites in 2D materials.
- Typical defects are chalcogen (S, Se, Te) vacancies.

Se:W ratio has significant impact on domain size, shape, and “defect” formation.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Time (min)</th>
<th>Pre-Anneal</th>
<th>Pressure (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>30</td>
<td>500°C, 15min</td>
<td>700</td>
</tr>
</tbody>
</table>

Se:W Ratio: 170

Se:W Ratio: 400

Se:W Ratio: 800

Se:W Ratio: 14000
WSe$_2$ on Free Standing Graphene Templates

Nasim Alem, Josh Robinson

A. Azizi, et al. ACS Nano (in press)
WSe$_2$ – Epitaxy and Defects

(a) TEM image and (b) SAD pattern showing epitaxial relationship between WSe$_2$ and graphene
(c) Structural model showing alignment of W atoms in WSe$_2$ and C atoms in graphene (circled in red)

(a) HAADF-STEM image of monolayer and multilayer WSe$_2$
HAADF-STEM images of (a) monolayer WSe$_2$ and (b) edge region showing W-termination
d) TEM image showing nucleation near grain boundary in graphene
High-mobility three-atom-thick semiconducting films with wafer-scale homogeneity

Kibum Kang\textsuperscript{1,}\textsuperscript{*}, Saien Xie\textsuperscript{2,}\textsuperscript{*}, Lujie Huang\textsuperscript{1}, Yimo Han\textsuperscript{2}, Pinshane Y. Huang\textsuperscript{2}, Kin Fai Mak\textsuperscript{3,4}, Cheol-Joo Kim\textsuperscript{1}, David Muller\textsuperscript{2,3} & Jiwoong Park\textsuperscript{1,3}

t_0=26 hours
Watch Nokia Morph video:

What properties are important for flexible electronics?
Why 2D materials?

Graph showing mobility (cm²/V·s⁻¹) for different materials:
- Pentacene
- M-Oxide
- s-MD
- Poly-Si
- CNT TFT
- s-TMD
- sc-Si
- Phosphorene
- III-V
- Graphene

Another graph showing strain limit (%):
- III-V
- M-Oxide
- sc-Si
- Pentacene
- CNT
- s-TMD
- Graphene

Graph showing channel thickness of flexible FET (nm) and higher frequency (cm²/V·s⁻¹):
- Graphene monolayer
- WSe₂ monolayer
- InAs TFT
- Phosphorene multilayer
- CNT TFT
- ZnO
- GaAs NW
- Si ribbons

Legend:
- Nanomaterials
- Bulk materials

Remarks:
- Greater flexibility, transparency, and gate control
# Properties of selected 2D materials

## Table 1: Room temperature solid-state properties of selected 2D crystalline materials.

<table>
<thead>
<tr>
<th>2D Material</th>
<th>Optical</th>
<th>Electrical</th>
<th>Mechanical</th>
<th>Thermal</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Band gap (eV)</td>
<td>Device Mobility (cm² V⁻¹ s⁻¹)</td>
<td>vₚ₀sat (cm s⁻¹)</td>
<td>Young’s Mod. (GPa)</td>
<td>Fracture strain (%)</td>
</tr>
<tr>
<td>Graphene</td>
<td>0</td>
<td>10³−5 × 10⁴</td>
<td>1−5 × 10⁷</td>
<td>1,000</td>
<td>27−38 (25)</td>
</tr>
<tr>
<td>1L MoS₂</td>
<td>1.8</td>
<td>10−130</td>
<td>4 × 10⁶</td>
<td>270</td>
<td>25−33 (23)</td>
</tr>
<tr>
<td>Bulk MoS₂</td>
<td>1.2</td>
<td>30−500</td>
<td>3 × 10⁶</td>
<td>240</td>
<td>NA</td>
</tr>
<tr>
<td>1L WSe₂</td>
<td>1.7</td>
<td>140−250</td>
<td>4 × 10⁶</td>
<td>195</td>
<td>26−37 (NA)</td>
</tr>
<tr>
<td>Bulk WSe₂</td>
<td>1.2</td>
<td>500</td>
<td>NA</td>
<td>75−100</td>
<td>NA</td>
</tr>
<tr>
<td>h-BN</td>
<td>5.9</td>
<td>NA</td>
<td>NA</td>
<td>220−880</td>
<td>24 (3−4)</td>
</tr>
<tr>
<td>Phosphorene</td>
<td>0.3−2*</td>
<td>50−1,000</td>
<td>NA</td>
<td>35−165</td>
<td>24−32</td>
</tr>
</tbody>
</table>

h-BN: hexagonal boron nitride; NA: not available; 2D: two-dimensional.
All listed values should be considered estimates. In some cases, experimental or theoretical values are not available (NA).

*The precise value for the bandgap, which is a maximum for a monolayer is a matter of ongoing research.
The || symbol signifies the in-plane direction; ⊥ signifies the out of plane direction.
2D Thin Film Transistors

Figure 4 | High-performance room-temperature 2D TFTs. (a) Transfer characteristics of a multilayer MoS$_2$ FET (W/L = 3/1 mm) with high-k gate dielectric featuring an on/off switching ratio > $10^7$ and sub-threshold slope (SS) of $\sim$ 82 mV per decade fairly close to the ideal limit of 60 mV per decade. Inset is a schematic of the flexible device. (Adapted, with permission, from ref. 17 (copyright 2013 American Chemical Society.).) (b) Conductivity as a function of gate voltage for four MoS$_2$ devices on PMMA surfaces. The peak field-effect mobilities are 30, 68 and 480 cm$^2$/V·s, corresponding to MoS$_2$ thicknesses of 1.5, 6.5 and 47 nm, respectively. Reproduced, with permission, from ref. 62 (copyright 2013, AIP Publishing LLC.). (c) Estimated (intrinsic) transit frequency of TMDs based on equation (1) and constant-field channel length scaling. The low- and high-field limits are determined by the low-field mobility ($\mu_L \sim 30$ cm$^2$/V·s$^{-1}$, $f_T \sim 0.4$ GHz·um$^{-1}$) and saturation velocity ($v_{sat} \sim 4 \times 10^6$ cm·s$^{-1}$, $f_T \sim 6$ GHz·um$^{-1}$) respectively. (d) Reported carrier mobility (four-terminal, black circles; two-terminal, red circles) and drain current modulation (blue triangles) of phosphorene FETs of varying thicknesses. The dashed lines are derived from modelling. (Adapted from ref. 28.) (e) Mechanical studies of flexible MoS$_2$ FETs. Below 2 mm bending radius, the exponential increase in off current is due to cracks in the gate dielectric shown in the inset. (f) Similarly, the on current degrades, but primarily owing to buckling and delamination, which is thickness dependent. Inset is an illustration of device buckling. (e,f) © 2013 IEEE. Reproduced, with permission, from ref. 58.
Heterostructure devices

Figure 5 | Flexible 2D heterostructure devices. (a) Output characteristics of a TFT consisting of a graphene/h-BN channel/dielectric heterostructure stack on PI substrate showing soft current saturation and high current density. Gr: graphene. (© 2013 IEEE. Reproduced, with permission, from ref. 39.) (b) Transfer curves of a transparent trilayer TFT with a MoS$_2$ channel, h-BN gate dielectric and few-layer graphene gate electrode on PEN substrate featuring robust electronic properties under different bending conditions up to 1.5% strain. The inset shows the schematic diagram of the flexible device. Adapted, with permission, from ref. 18 (copyright 2013 American Chemical Society). (c) Room-temperature tunnel current of a five-layer flexible heterostructure vertical tunnel transistor. The data shown are at zero gate voltage and 20 mm bending radius. WS$_2$ thickness is around 3-10 layers. Schematic of the vertical transistor is shown in the inset. (Adapted from ref. 66.) (d) Simplified illustration of the proposed ideal integrated heterogeneous flexible device structure, which employs graphene for RF electronics and semiconducting TMDs or phosphorene for low-power complementary digital and analogue devices. h-BN is ideal as a multifunctional gate dielectric for mobility enhancement, high velocity saturation and thermal management of the channel heat based on its desirable anisotropic thermal conductivity ($\lambda$). A hydrophobic coating can preserve device performance. The embedded back-gate process can enable multiple gate fingers, low gate resistance and high current density. HI refers to an heat insulator.
Figure 7 | Large-scale nanomanufacturing. (a) A scheme for continuous R2R growth of graphene based on selective Joule heating of copper foil. Gr: graphene. (b) The growth is followed by R2R coating and bonding to PET, and finally, the spray etching of the copper substrate to manufacture 100 m long transparent conductive graphene/plastic rolls. (c) Large-scale manufacturing of graphene has enabled smart phones with graphene touch screens, which are now sold in China (Image courtesy of 2D Carbon Tech). (d) Experimental demonstration of electrochemically delaminated graphene onto PI that affords reuse of Cu foil for a sustainable nanomanufacturing technology. Inset is an illustration of the electrochemical method. Reproduced, with permission, from ref. 74 (© 2013 WILEY-VCH Verlag & Co. KGaA, Weinheim). (e) Simplified technology maturity perspective for flexible 2D nanotechnology. Growth, transfer and circuits based on graphene have been demonstrated leading to the 2013–2014 market penetration of graphene as smart phone touch panels. The large-scale advancement of graphene is expected to benefit the progress of other 2D sheets, and graphene’s market penetration can be a launch pad for the commercial development of fully integrated flexible smart systems using 2D materials for both passive and active devices. (a,b) Reproduced with permission from ref. 73. (copyright 2013, AIP Publishing LLC).