Looking at Atoms
An Overview of Advanced Characterization Techniques for 2D Materials

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The TMD Synthesis “Atlas”

Metal Transformation

"Soft Chalcogenization"

\[
M_{(s)} + X_{2(g)} \rightarrow MX_2
\]

Natural Bulk Crystals

Chem/Mech Exfoliation

Chemical Vapor Transport

Bulk Crystal Formation

\[
M_{(s)} + 2X_{(s)} + \text{Transport Agent} \rightarrow MX_2 + TA_{(s)}
\] (Br₂ or I₂)

Chemical Vapor Deposition

Solid State Reactions

\[
M_{(s)} + X_{2(s)} \rightarrow MX_2
\]

Heat

Transition Metal Dichalcogenide

(MX₂)

Powder Vaporization

Molecular Beam Epitaxy

Electrochemical Synthesis

Pulsed Laser Deposition

Spray Pyrolysis

Typical Carrier: H₂/N₂/Ar

Metal Organic Precursors

MoO₃ + H₂S
MoCl₅ + H₂S
MoCl₃ + S₂

W(CO)₆ + (CH₃)₂Se
WC₅ + H₂Se

Temp = 200-1100°C
P = 1 - 760 Torr

P = 1 - 760 Torr
T = 600 - 950°C

Annual Review of Materials Research, 45(1).
Grow it... Then, look at it.

Microscopy

Optical Microscopy

Atomic Force Microscopy

Scanning Electron Microscopy

Raman Spectroscopy

E_{2g} \quad A_{1g}

1st L

2nd L

MoS_2

Raman is thickness dependent.

Photoluminescence

PL is thickness dependent.

Typical Techniques

Atomic Force Microscopy

Scanning Electron Microscopy

Optical Microscopy

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Raman Spectroscopy

- Characteristic Raman frequencies
- Changes in frequency of Raman peak
- Polarisation of Raman peak
- Width of Raman peak
- Intensity of Raman peak

TMDs at the Atomic Scale

Transmission Electron Microscopy

Watching Defects

NATURE COMMUNICATIONS | DOI: 10.1038/ncomms5867

2D Crystal Consortium
NSF Materials Innovation Platform
Atomic Transformations

Powder Vaporization

Not the Whole Story

High MoO$_x$: S$_2$ Ratio
Vertical Fins

Low MoO$_x$: S$_2$ Ratio
Lateral Domains

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

2D Crystal Consortium
NSF Materials Innovation Platform

2D Materials 3 (4), 041003
Atomic Transformations

Two Regimes for TMD Growth

- $P_{\text{MoO}_3} > P_{\text{S}_2}$
  - I. Reduction
  - II. Adsorption
  - III. Nucleation
  - IV. Lateral Growth

- $P_{\text{MoO}_3} < P_{\text{S}_2}$
  - I. Sulfurization
  - II. Adsorption
  - III. Nucleation
  - IV. Vertical Growth

Electron Diffraction
EDX
Building Structure Models

Simulations: xHREM software package

Building Electronic Models

Physical Structure

Electronic Structure

Dimethylselenium (DMSe) + Hydrogen Selenide (H₂Se)

Theory:
\[ \text{W(CO)}_6 + \text{Se(CH}_3)_2 + 2\text{H}_2 \rightarrow \text{WSe}_2 + 6\text{CO} + 2\text{CH}_4 + \text{H}_2 \]
\[ \text{W(CO)}_6 + \text{H}_2\text{Se} + \text{H}_2 \rightarrow \text{WSe}_2 + 6\text{CO} + \text{H}_2 \]

Experiment:
\[ [\text{W(CO)}_6 + ?] + [\text{Se(CH}_3)_2 + ?] + 2\text{H}_2 \rightarrow \text{WSe}_2 + 6\text{CO} + 2\text{CH}_4 + \text{H}_2 + ? \]
\[ [\text{W(CO)}_6 + ?] + [\text{H}_2\text{Se} + ?] + \text{H}_2 \rightarrow \text{WSe}_2 + 6\text{CO} + \text{H}_2 + ? \]

Growing WSe₂
Eliminating some “MO”

Raman, XPS: require ~% level impurities to be useful… BUT impurity levels of ppm can influence electronic properties

DMSe = Carbon Contamination
ICP-Mass Spectroscopy

http://www.jfe-tec.co.jp/en/battery/analysis/material/la-icp-ms.html
Evaluating Precursor Impact

ICP-MS provides a means to evaluate trace impurities in the synthesized 2D layer.

Unpublished, with Wallace Group @ UT-Dallas
TOF-SIMS

- Excite a sample surface with a finely focused ion beam
- Secondary ions and ion clusters to be emitted from the samples surface
- Time-of-flight analyzer used to measure the exact mass of the emitted ions and clusters
- From the exact mass and intensity of the SIMS peak, the identity of an element or molecular fragments can be determined.
Chemical mapping of residue
Chemical Mapping of Dopants

Mo Elemental Map

Mn Elemental Map

MoS$_2$

SiO$_2$

10 µm

10 µm

DOI: 10.1021/acs.nanolett.5b02315
Atomic Scale Surface Chemistry

Graphene interface

h-BN

Normalized yield

Depth (nm)

Normalized yield

Advent. matl.

Graphene

(NH₄)₂S₂O₈ residues

C₂H₂O residue

Cu foil residue

Chemisorbed advent. matl.

h-BN

C₃⁻

C⁻

CB⁻

¹⁰BB⁻

Normalized yield

0.9 nm

0.38 nm
Atomic mixing between graphene and substrates

The problem with roughness

Before & After 35 seconds of Cs+
1986 Nobel Prize

Scanning Tunneling Microscopy

Atomic-Scale Electronic Properties

STM tip apex

Tip Motion

Tip Trace over surface

Tunneling current and tip-Sample Distance D

Sample Surface

Tip-sample Bias Voltage V and current measurement I

Nobel Laureates Heinrich Rohrer and Gerd Binnig

Encyclopedia of Nanotechnology; Editors: Professor Bharat Bhushan
Scanning Tunneling Spectroscopy

\[ I \sim e^{-kz} \int_0^{eV} dE \cdot LDOS_{Sample}(E_F + E) \]

\[ \frac{dI}{dV} \bigg|_V \sim LDOS_{Sample}(E_F + eV) \]

- At a given \((x, y)\):
  \[ \frac{dI}{dV} (V) = \text{local DOS} \]

- At a given \(V\):
  map \((x, y)\) of \(dI/dV = \text{LDOS map at } V\)
The Bandgap of TMDs
Excitons

Spatial map of the exciton wavefunction corresponding to the excitonic peak labelled A in a–c (wavefunction is shown with the hole (black circle) fixed in space).

Mo atoms are small black squares, Se atoms not shown.

TMD excitons are 5-100x higher energy than traditional semiconductors

http://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_5/advanced/t5_1_3.html
Complex 2D Structures

Lin et al., Nature Communications, 2015; 6: 7311 DOI: 10.1038/ncomms8311
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Raman
- Rapid ID of structure & chemistry

TEM/STEM
- Atomic-scale structural/chem properties

TOF-SIMS
- Atomic-scale surface elemental analysis

Photoluminescence
- Rapid ID of optical properties

ICP-MS
- Trace Impurity Levels

STM/STS
- Atomic-scale electronic properties

Raman shift (cm\(^{-1}\))

- WSe\(_2\)
- H\(_2\)Se
- DMS\(_2\)

Intensity (A.U.)

- C-1338
- C-1690

Photoluminescence spectrum

- Interband
- WSe\(_2\)
- MoS\(_2\)

- 1.83 eV
- 1.59 eV
- 1.65 eV
An NSF user facility with broad access to Synthesis, Characterization, and Theory of 2D Materials for Electronic Applications.

mip.psu.edu

• 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