2DCC Framework… where we fit in!

- **Ellipsometry**
- **Raman Spectroscopy**
- **Photoluminescence**

**IN-SITU CHARACTERIZATION**
- STM/AFM
- ARPES
- 4-Probe Testing
- Raman Spectroscopy
- Photoluminescence

**SYNTHESIS**
- Hybrid MBE
- Chalcogenide
- MOCVD
- Bulk Growth

**2D MATERIALS**
- DFT
- Monte Carlo
- Molecular Dynamics
- Reactive Force Field
- Phase Field

**THEORY / SIMULATION**

- Gas Source
- Chalcogenide
- CVD

mip.psu.edu
Thin Film - MOCVD Personnel

Faculty

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GaSe

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NbS$_2$, Epi-graphene

Xiaotian Zhang
WSe$_2$

Jeffrey Kronz
CVD Graphene

Kehao Zhang
Powder Vaporization MoS$_2$
Layered materials….beyond graphene

Wide range of electronic properties

Transition metal dichalcogenides (TMDs)
MoS$_2$, WSe$_2$, WS$_2$, MoSe$_2$, WTe$_2$, etc.

Covalent bonds within layer

Layers held together by van der Waals forces

Bulk Crystals

Films

Can form stable monolayer and few layer films

Layer number-dependent properties

Photoluminescence spectra

Energy band structure

Heterostructures without lattice matching

Valley polarization

σ+

σ−

Conduction band

K

K'

Interlayer exciton coupling

Coulomb engineering

σ+

σ−

Valence band

Xiao, et al.

P. Rivera et al.
Nature Comm. 6 (2015) 6242

A. Raja, et al.
Nature Comm. 6 (2017) 15251

A.K. Geim and I.V. Grigorieva
Nature 499 (2013) 419

A. Splendiani, et al.
Nano Lett 10 (2010) 1271
2D tunnel diodes and transistors

T. Roy, et al.

Flexible electronics

Tom Jackson (PSU)

Exfoliated MoS$_2$

M. Jariwala, et al.

Excitonic transistors

Saptarshi Das (PSU)

Thin film photovoltaics

Linyou Cao

Chem/bio sensors

F. Perkins, et al.
2D TMDs – How to get monolayers?

Exfoliation of bulk crystals

$15 \times 22 \text{ mm MoS}_2 (\$300) - 2dsemiconductors.com$

Powder vapor transport

$F. \text{ Zhang, et al. 2D Materials 4 (2017) 025029}$
Sources (liquid and solid) are outside chamber in temperature and pressure-controlled “bubblers” to precisely control source vapor pressure. **Pyrophoric!**

Hydride gases (SiH$_4$, NH$_3$, AsH$_3$, H$_2$Se, H$_2$S, etc.) are used to minimize carbon incorporation. **Highly toxic!**

Vent/run assembly – used to establish steady state gas flows and switching.

Reaction chamber – typically cold wall to prevent source pre-reaction.

Pressure control of chamber – typically from milliTorr to atmospheric pressure.

Ventilating enclosure with toxic gas & flame detectors

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2016 2DCC Webinar: MOCVD Growth of 2D Chalcogenides: Challenges and Opportunities
Gas Source CVD/Metalorganic CVD

- Cold wall vertical and horizontal reactor designs
- CFD simulations used to model fluid, heat and mass transport

H₂ Carrier Gas
W, Mo, S, Se Precursors

- Focused on understanding impact of precursor chemistry on growth and properties of TMD films

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Gas Velocity (cm/s)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>700</td>
</tr>
</tbody>
</table>

Tungsten \( W(CO)₆, WCl₆ \)
Molybdenum \( Mo(CO)₆ \)
Niobium \( NbCl₅ \)
Selenium \( (CH₃)_₂Se, H₂Se \)
Sulfur \( (C₂H₅)₂S, H₂S \)
Substrates for TMD “Epitaxy”

MoS$_2$ on (0001) sapphire


<table>
<thead>
<tr>
<th>Substrate/Film</th>
<th>$a$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sapphire</td>
<td>0.476</td>
</tr>
<tr>
<td>SiC</td>
<td>0.307</td>
</tr>
<tr>
<td>GaN</td>
<td>0.319</td>
</tr>
<tr>
<td>hBN</td>
<td>0.250</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>0.316</td>
</tr>
<tr>
<td>WS$_2$</td>
<td>0.316</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>0.332</td>
</tr>
</tbody>
</table>

Mismatch~0.4%

(3x3) MoS$_2$/(2x2)Al$_2$O$_3$

Mismatch~13%

MoS$_2$ on (0001) GaN


Monolayer MoS$_2$

Sapphire
Epitaxial growth of large area TMD monolayers

- Growth of **large area, single crystal** TMD monolayers and heterostructures needed to advance device technologies

**Challenges/requirements:**

- Transition metals and chalcogens have very different vapor pressures
- Suitable substrate needed to provide template for “epitaxy”
- Growth conditions must promote lateral growth of domain edges with minimal bilayer nucleation

<table>
<thead>
<tr>
<th>Element</th>
<th>Melting Temp (°C)</th>
<th>Vapor Press (Torr) @500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>3422</td>
<td>1.78x10^{-47}</td>
</tr>
<tr>
<td>Mo</td>
<td>2617</td>
<td>1.97x10^{-27}</td>
</tr>
<tr>
<td>Nb</td>
<td>2468</td>
<td>2.97x10^{-38}</td>
</tr>
<tr>
<td>S</td>
<td>115</td>
<td>&gt;750</td>
</tr>
<tr>
<td>Se</td>
<td>221</td>
<td>49</td>
</tr>
<tr>
<td>Te</td>
<td>450</td>
<td>0.91</td>
</tr>
</tbody>
</table>

epitaxial orientation → lateral domain growth → coalescence
Three Step Process for WSe$_2$ Monolayers

Substrate temperature: 800˚C, H$_2$Se flow rate 7 sccm (Se/W~26,000), Reactor pressure: 700 Torr

Nucleation Stage:
- High initial partial pressure of W(CO)$_6$ to drive nucleation.

Ripening Stage:
- Annealing in H$_2$Se to promote surface diffusion and uniform WSe$_2$ domain size.

Lateral Growth Stage:
- Lower partial pressure of W(CO)$_6$ to enable lateral domain growth without additional nucleation.

Ripening of WSe$_2$ islands

Nucleation stage: 30 sec at W(CO)$_6$=1.2x10$^{-3}$ sccm, H$_2$Se=7 sccm, 800°C, 700 Torr

Ripening stage: 0 to 45 mins at H$_2$Se=7 sccm only
Ripening and Surface Diffusion

- Diffusing species may be adatoms or small clusters

2D Ripening Model:

**Domain size \( r(t) \):**

\[
r(t) = r(0) \left(1 + \frac{t}{\tau}\right)^{1/3}
\]

**Cluster density \( \rho \):**

\[
\rho(r = 0, t) = \rho(r = 0,0) \frac{1}{1 + \frac{t}{\tau}}
\]

Estimate of surface diffusion coefficient:

\[
L_D = 2\sqrt{Dt} \\
L_D \approx \frac{1}{2} L_{av} \text{ where } L_{av} \approx \sqrt{1/\rho}
\]

\[
\rho \approx \frac{1}{16Dt}
\]

\[
D \approx 1.2 \times 10^{-14} \text{ cm}^2/\text{sec}
\]

*similar to Pt cluster diffusivity on sapphire at 600°C (P. Wynblatt, et al. Prog. Solid State Chem 9, 21 (1975)).
Lateral Growth of WSe$_2$ Islands

Nucleation stage: 30 sec at $\text{W(CO)}_6=1.2\times10^{-3}$ sccm, $\text{H}_2\text{Se}=7$ sccm, 800$^\circ$C, 700 Torr

Ripening stage: 10 mins at $\text{H}_2\text{Se}=7$ sccm only

Lateral growth stage: 5-45 mins at $\text{W(CO)}_6=2.7\times10^{-4}$ sccm, $\text{H}_2\text{Se}=7$ sccm, 800$^\circ$C, 700 Torr

- Coalescence of monolayer in < 1 hour
- Bilayer growth rate increases after ~50% monolayer coverage
- Preferred direction
- Commensurability
Lateral Growth – Effect of Substrate Temperature

- Lateral growth rate independent of temperature from ~700-900°C
- Suggests growth limited by mass transport of W-precursor to surface
- Shape evolution related to Se:W ratio
- Increase H₂Se to 10 sccm

Nucleation stage: 30 sec at W(CO)₆=1.2x10⁻³ sccm, H₂Se=7 sccm, 800°C, 700 Torr
Ripening stage: 10 mins at H₂Se=7 sccm only, 800°C, 700 Torr
Lateral growth stage: 10 mins at W(CO)₆=2.7x10⁻⁴ sccm, H₂Se=7 sccm, 600-900°C, 700 Torr

S. Wang, Chem. Mater. 2014, 26 (22), 6371–6379
Epitaxial Orientation – In-Plane XRD

- Conventional Bragg-Brentano XRD challenging for 2D monolayers

Epitaxial Relationship: \((1\bar{1} \bar{2}0)_{\text{WSe}_2} \parallel (1\bar{1} \bar{2}0)_{\text{sapphire}}\)

TEM Characterization of WSe$_2$

- Water-based transfer process used to remove WSe$_2$ from sapphire
  (developed by Fu Zhang and Nasim Alem at Penn State)

- Anti-phase boundaries in WSe$_2$ due to coalescence of 0° and 60° domains

Grain boundaries in TMD monolayers

$0^\circ + 60^\circ$ → anti-phase grain boundary (metallic)
$0^\circ + 0^\circ$ → perfect crystal

H. Yu et al. Small 2017, 13, 1603005
Epitaxy of WSe$_2$ on hBN flakes

Three-step growth: 60 sec. nucleation, 10 mins ripening, 45 mins lateral growth at 800$^\circ$C, 7 sccm H$_2$Se

Fu Zhang and Nasim Alem

Reduced number of anti-phase grain boundaries for WSe$_2$ on hBN
Photoluminescence

**WSe₂ on sapphire**

*Image showing AFM imaging and PL spectrum.*

- **Energy (eV):** 1.45, 1.50, 1.55, 1.60, 1.65, 1.70, 1.75
- **Normalized Intensity (a.u.):** 1.64, 1.62, 1.60
- **FWHM:** ≈ 90-130 meV
- **PL peak:** 1.606 ± 0.017 eV

**WSe₂ on hBN**

*Image showing AFM imaging and PL spectrum.*

- **Energy (eV):** 1.45, 1.50, 1.55, 1.60, 1.65, 1.70, 1.75
- **Intensity (a.u.):** FWHM ≈ 55 meV
- **PL peak:** 1.656 ± 0.002 eV

*Further discussion*

Promising approach but limited by lack of large area hBN substrates or templates.
Process scale-up
Upgraded III-V MOCVD system - Converted to chalcogenides

Glove box for sample loading/unloading
Integrated toxic gas detection system
Gas panel with vent/run manifolds, 6 bubbler for liquid/solid sources, 4 gas source lines (H₂Se, H₂S)
Cold wall reactor for 2” diameter substrates with rotation

Material capabilities:
- WS₂, MoS₂, NbS₂
- WSe₂, MoSe₂, NbSe₂
- WTe₂, MoTe₂
- Doping, alloys, heterostructures
WS$_2$ epitaxy on sapphire

Pressure: 50 Torr, Duration: 60 min, $W(\text{CO})_6 = 5.7 \times 10^{-4}$ sccm, $H_2S = 160-320$ sccm

The chalcogen concentrations plays an important role in obtaining epitaxy.
(Mo,W)S\textsubscript{2} monolayers, alloys and heterostructures

Growth temperature: 850-1000°C, Reactor Pressure: 50 Torr, \( W(CO)\textsubscript{6} = 10^{-4}-10^{-5}\) sccm, \( Mo(CO)\textsubscript{6} = 10^{-3}-10^{-2}\) sccm \( H\textsubscript{2}S = 400\) sccm, \( H\textsubscript{2}\) carrier gas

AFM: WS\textsubscript{2} on sapphire

In-Plane XRD: WS\textsubscript{2} on sapphire

Photoluminescence: (Mo,W)S\textsubscript{2}

MoS\textsubscript{2}/WS\textsubscript{2} heterostructures

ADF-STEM image (S. Bachu, D. Hickey and N. Alem)
Defect mediated growth

Pristine Plasma treated

Pressure: 50 Torr, Duration: 20 min, W(CO)$_6$ = 5.7 x 10$^{-4}$ sccm, H$_2$S = 400 sccm

Epitaxial graphene

Growth of TMD

In collaboration with Prof. Joshua Robinson, Prof. Adri van Duin and Prof. Eric Hudson (PSU)

Study interaction of defects with precursors to control nucleation sites.
Reactor modelling and simulations

ReaxFF calculations of gas phase kinetics – Prof. Adri van Duin
CFD simulations Prof. Yuan Xuan (PSU)

Modelling of gas phase chemistry and flow dynamics to develop predictive capacity
In-situ Characterization

Installation Mid 2018

Features

- Cold wall stainless steel chamber
- 2 inch wafer growth with mechanical wafer rotation
- Transfer chamber with robot arm to transfer sample between chambers
- Ellipsometer for *in-situ* growth monitoring
- Additional analysis chamber for Raman/PL without ambient exposure

<table>
<thead>
<tr>
<th>Precursor gas lines</th>
<th>Tungsten</th>
<th>W(CO)$_6$, WCl$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Molybdenum</td>
<td>Mo(CO)$_6$</td>
</tr>
<tr>
<td></td>
<td>Niobium</td>
<td>NbCl$_5$</td>
</tr>
<tr>
<td></td>
<td>Selenium</td>
<td>(CH$_3$)$_2$Se, H$_2$Se</td>
</tr>
<tr>
<td></td>
<td>Sulfur</td>
<td>(C$_2$H$_5$)$_2$S, H$_2$S</td>
</tr>
</tbody>
</table>
A national user facility focused on advancing the synthesis of 2D chalcogenides

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 U.S. academic or government use
- Access to a team of local experts
- Webinars, workshops, website resources
- Partnership opportunities with PUI, MSI

External user requests: Mono/Bilayer WS$_2$, MoS$_2$, WSe$_2$.

Research proposals: Te based TMDs will be explored.

in-situ characterization equipment

For more information:  mip.psu.edu