Large Area Synthesis of Mono- and Multi-layer MoS$_2$ for 2D Nanoelectronics

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Thin Body

Thin silicon required: Minimize short channel effects

\[ L_{G,\text{min}} \sim 0.653 \left[ t_{Si} + 2(\epsilon_{si} / \epsilon_{ox})t_{ox} \right] \]

<table>
<thead>
<tr>
<th>( t_{Si} ) (nm)</th>
<th>( L_{G,\text{min}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>6.4</td>
</tr>
<tr>
<td>4</td>
<td>5.1</td>
</tr>
<tr>
<td>2</td>
<td>3.8</td>
</tr>
<tr>
<td>1</td>
<td>3.2</td>
</tr>
</tbody>
</table>

\[ L_{G,\text{min}} \text{ (FinFET)} = 1.5 \times L_{G,\text{min}} \text{ (GAA)} \]
\[ t_{ox} = 3 \text{ nm}, \ EOT = 0.65 \text{ nm} \]

Low mobility \( \rightarrow \) Low performance

[\( \mu \) data: Gomez/Hoyt IEEE EDL 07, Uchida IEDM 02]
Formation of Heterostructures for TFETs

- Staggered Gap (type II)
- Broken Gap (type III)

w/ Gate Modulation

Thin Channel Trade-Off
Mobility & Band Gap vs. Electrostatics


Source: Eric Pop (Stanford)
Thin Channel

Average roughness ≈ 0.2 nm mobility $\propto$ (thickness)$^6$

“I would personally believe that any magical technology to realize extremely-flat surfaces could be available in the future.” – S. Takagi

K. Uchida (Toshiba), IEDM ‘03

S. Takagi (U Tokyo), IEDM ‘10
4-5 Layer MoS$_2$ Side Edge

Collaboration: Molecular Foundry, LBNL
# 2D Layered Atomic Crystals

<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>Semiconducting dichalcogenides: MoTe$_2$, WTe$_2$, ZrS$_2$, ZrSe$_2$ and so on</td>
<td>Metallic dichalcogenides: NbSe$_2$, NbS$_2$, TaS$_2$, TiS$_2$, NiSe$_2$ and so on</td>
<td>Layered semiconductors: GaSe, GaTe, InSe, Bi$_2$Se$_3$ and so on</td>
<td></td>
</tr>
<tr>
<td>2D oxides</td>
<td>Micas, BSCCO</td>
<td>MoO$_3$, WO$_3$</td>
<td>Perovskite-type: LaNb$_2$O$_7$, (Ca,Sr)$_2$Nb$<em>3$O$</em>{10}$, Bi$_4$Ti$<em>3$O$</em>{12}$, Ca$_2$Ta$<em>2$TiO$</em>{10}$ and so on</td>
<td>Hydroxides: Ni(OH)$_2$, Eu(OH)$_2$ and so on</td>
<td></td>
</tr>
<tr>
<td>Layered Cu oxides</td>
<td>TiO$_2$, MnO$_2$, V$_2$O$_5$, TaO$_3$, RuO$_2$ and so on</td>
<td></td>
<td></td>
<td>Others</td>
<td></td>
</tr>
</tbody>
</table>

Mono- or Multi-layer MoS$_2$?

- Several experimental results confirm that multi-layer MoS$_2$ generally have better electronic properties.

Li et al., Nano Lett. (2013) Tsukagoshi group, Tsukuba, Japan

Li et al., ACS Nano (2014) Tsukagoshi group, Tsukuba, Japan

S. Das et al., Nano Lett. (2013) Appenzeller group, Purdue
Relative peak intensity ratio of MoS$_2$ peaks (near 400 cm$^{-1}$) vs the silicon peak (near 520 cm$^{-1}$) is higher for multilayer MoS$_2$. Scale bar: 100µm.
Contents

- CVD Basics
  - Precursor Diffusion/Deposition Kinetics
- Multi-layer MoS$_2$ Growth
  - Pressure and Temperature Dependence
- Single-layer MoS$_2$ Growth
  - Seeded 1L/Non-seeded 1L Growth
- Alternative MoS$_2$/TMD Growth Methods
  - ALD, MOCVD
Chemical Vapor Deposition (CVD) Setup for MoS$_2$ Growths

- Vacuum to ATM pressure growth capability
- External heating belt for constant temperature sulfur heating

$$2 \text{ MoO}_3 (g) + 4 \text{ S} (g) \rightarrow 2 \text{ MoS}_2 (s) + 3 \text{ O}_2 (g)$$
Precursor Diffusion/Deposition Kinetics

Substrate

Surface Diffusion
Surface Reactions

Adsorption

Desorption

Diffusion

MoS\textsubscript{2}

Reaction

Diffusion

MoO\textsubscript{3}

Forced-Convection Region

Argon/Sulfur

Surface-Phase Processes

Gas-Phase Processes

Argon/Sulfur
Precursor Diffusion/Deposition Kinetics

Gas Molecule MFP

$$\lambda \,(cm) = 2.33 \times 10^{-20} \frac{T(K)}{\xi^2(cm^2)P\,(torr)}$$

$$\xi = \text{gas molecule diameter} \quad \lambda \propto \frac{T}{P}$$

Gas Diffusion Coefficient

$$D \,(cm^2/s) = D_0 \left( \frac{T(K)}{273\,K} \right)^n \frac{760\,torr}{P\,(torr)}$$

$$1.5 < n < 2 \quad D_0 \sim 1\,cm^2/s \quad D \propto \frac{(T)^n}{P}$$

Molecular Flow in a Tube

Viscous Flow in a Tube

Precursor Diffusion/ Deposition Kinetics

Gas Molecule MFP
\[ \lambda (\text{cm}) = 2.33 \times 10^{-20} \frac{T(K)}{\xi^2 \text{ (cm}^2\text{)} P(\text{torr})} \]

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\[ 1.5 < n < 2 \]

\[ D_0 \sim 1 \text{ cm}^2/\text{s} \]

\[ D \propto \frac{(T)^n}{P} \]

Good precursor/ gas flow control: Need to operate in viscous flow regime.

Effect of Temperature and Pressure on Deposition Rate

Temp and Pressure Control:

- High T, Low P
  - High Diffusivity
  - High MFP
  - Increased Deposition Rate
- Low T, High P
  - Low Diffusivity
  - Low MFP
  - Decreased Deposition Rate

Two Limits for CVD Growth:

- Fast Surface Reaction
  - High Sc
  - Mass-Transport Limited Growth
- Slow Surface Reaction
  - Low Sc
  - Surface-Reaction Limited Growth

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Pressure and Temperature Dependent ML MoS$_2$ Growth

10 torr 600°C  Increase Temperature  675°C

700 torr

MoO$_3$: 5-6 mg, S Heating Belt: 250°C, Ar Flow: 400 sccm

285 nm SiO$_2$/Si Chips: 2 cm x 2.5 cm
Pressure and Temperature Dependent ML MoS\textsubscript{2} Growth

10 torr 600°C  Increase Temperature  675°C

700 torr

Pressure increase $\rightarrow$ Decrease MoO\textsubscript{3} sublimation/ partial pressure

285 nm SiO\textsubscript{2}/Si Chips: 2 cm x 2.5 cm
Pressure Dependent Raman Evolution and AFM

Excess MoO$_3$ Deposition
MoO$_3$ and MoS$_2$ mixed
Raman spectra

Thickness (AFM): 5.7 nm
~6-7 layers

- 10 torr
  520 cm$^{-1}$ Si Peak

- 200 torr
  E$_{1g}^1$ and A$_{1g}$ Separation: 23.56 cm$^{-1}$
  520 cm$^{-1}$ Si Peak

- 700 torr
  E$_{1g}^1$ and A$_{1g}$ Separation: 26.18 cm$^{-1}$
  Si Peak Signal Covered by Film

Bulk MoS$_2$ (~18-20 layers)
MoS$_2$ Raman Spectra – 1 to 4-layer Evolution

$E_{2g}^1$ typically red shifts, $A_{1g}^1$ peak blue shifts

Frequency separation for Bulk: $\sim 25$ cm$^{-1}$ for 6+ layers

4-5 Layer MoS$_2$ Side Edge

MoS$_2$ TEM Sample: $A_{1g}$-$E'_{2g}$
$\Delta f = 25.3$ cm$^{-1}$

4-5 MoS$_2$ Layers

Collaboration:
Molecular Foundry, LBNL
MoO$_3$ sublimation dominates around SiO$_2$/Si surface

Low Ambient (Ar) Pressure Regime

Fixed incoming P.P. of S: S inhibited from surface reaction

High Ambient (Ar, ATM) Pressure Regime

Fixed incoming P.P. of S: S fully reacts with Mo near surface

MoO$_3$ sublimation limited around SiO$_2$/Si surface
Pressure and Temperature Dependent ML MoS$_2$ Growth

Increase Temperature

10 torr 600°C  Increase Temperature  675°C

Increase Pressure

700 torr

200 torr, Vary Temperature

Temperature increase $\rightarrow$ Increase MoO$_3$ sublimation/ partial pressure

285 nm SiO$_2$/Si Chips: 2 cm x 2.5 cm
Temperature Dependent Raman Evolution and AFM

AFM film thicknesses thicker than corresponding Raman signals

$E_{2g}^1$ and $A_{1g}$ Peak Separation Evolution:

$20.94 \text{ cm}^{-1} \rightarrow 25.26 \text{ cm}^{-1}$

Pressure: 200 torr
Optimal ML MoS$_2$ Film for Applications

ML Film
Peak Separation: 24.63 cm$^{-1}$

\[ \Delta y = 2.6 \text{ nm} \]

\[ 715^\circ \text{C}, 700 \text{ torr}, \text{MoO}_3: \text{5-6 mg, S Heating Belt: } 250^\circ \text{C}, \text{Ar Flow: 400 sccm} \]

W/L = 60µm/0.5µm
Initial Transistor $I_{DS}$ vs $V_{DS}$ Curve

$W/L = 60 \ \mu m / 0.5 \ \mu m$

$V_{gs} = 0 - 14 \ \text{V}$

1V Increment

$I_{DS}$ (uA)

$V_{DS}$ (V)
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- **Alternative MoS\textsubscript{2}/TMD Growth Methods**
  - ALD, MOCVD
Seed Layers

- 2D TMDs do not grow well on pristine surfaces
  - Non-seeded growth starts on edges
  - **Nucleation sites** are needed

- Starting with 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA):
  - **PTCA** (… tetracarboxylic acid)
  - **PTAS** (PTCA tetrapotassium salt)

Sigma-Aldrich.
Comparison of MoS$_2$ Surfaces from PTCA and PTCDA

**Using PTCA**
forms single crystalline MoS$_2$ grains

**Using PTCDA**
forms nearly full coverage MoS$_2$ with many impurities on surface
Seed Layer Growth – PTCA

750 °C, 100 Torr, 200 sccm Ar SiO$_2$/Si Substrate

Δy = 0.74 nm

10 μm

500 nm
1L Raman Peak Separation for PTCA Seeded Growth

Peak Separation: 19.65 cm$^{-1}$

520 cm$^{-1}$ Si Peak

384.65 cm$^{-1}$ $E_{12g}$

404.30 cm$^{-1}$ $A_{1g}$
1L MoS$_2$ Raman Spectra Peak Difference

$E_{2g}^1$ typically red shifts, $A_{1g}^1$ peak blue shifts

Frequency separation for Bulk: $\sim$25 cm$^{-1}$ for 6+ layers

Seeded MoS$_2$ Growth

850 °C, ATM Pressure, 10 sccm Ar, SiO$_2$/Si Substrate

Collaboration: K. Smithe, Pop Lab

AFM: 1.3 nm, ~1-2 Layers MoS$_2$

520 cm$^{-1}$ Si Peak

Peak Separation: 21 cm$^{-1}$

$E_{2g}^1$: 382 cm$^{-1}$

$A_{1g}$: 403 cm$^{-1}$
PTAS Seeded MoS$_2$ Growth on 285 nm SiO$_2$/Si
Non-seeded Large-area ATM Single-crystalline Growth

Non-seeded MoS$_2$ Growth

Key: Precursor and gas flow control.
- MoO$_3$ uniformly dispersed onto precursor Si substrate
- External heater for sulfur
- Gas flow modulation

Overlapping MoS$_2$ Grains Regions

Single MoS$_2$ Grain Regions

Collaboration: Y. Chai, PolyU HK

"For Internal E3S Use Only. These Slides May Contain Prepublication Data and/or Confidential Information."
Consistency/ Uniformity of APCVD Growths

HK PolyU

Excess MoO$_3$ Sublimation

Excess Sulfur Reaction

Optimal Sulfur to MoO$_3$ Reaction

Hone Group (Columbia)

Dried Precursor MoO$_3$ on Si Substrate

van der Zande et al., Nature Materials, 12, 554 (2013)
Creating Hydrophilic/ Hydrophobic Surfaces (SiO₂/ Si)

O₂ Plasma Treated Surface
15.67° H₂O Contact, Hydrophilic

HMDS Treated Surface
70.00° H₂O Contact, Hydrophobic
Surface Treatment/ Functionalization for Promoting MoS$_2$ Growth

- **Seed Polymers**
  - PTAS, PTCA, PTCDA

- **Hydrophilic Surface Treatments**
  - Promote dispersion/ uniformity of:
    - Aqueous-based seeds
    - MoS$_2$ adsorbing onto surface
  - O$_2$ Plasma, Piranha, HF Dip

- **Highly Crystalline Substrate Surface**
  - Promote MoS$_2$ surface nucleation
  - More uniformity, epitaxial-like growth
MoS$_2$/ TMD CVD Growth Moving Forward

- **Optimize Precursor Control**
  - Steady precursor sublimation
  - Alternative higher vapor pressure/gaseous precursors
    - Better flow control

- **Optimize Temperature and Pressure Conditions**
  - Well controlled ambient conditions $\rightarrow$ **Consistent** film quality

- **Surface Treatment Methods for Promoting Growth**
  - Promote ordered surface nucleation $\rightarrow$ Improve crystallinity
  - Different growth mechanism for more uniformity
Alternative MoS$_2$/ TMD Growth Methods

Grown at 100°C
Precursors: Mo(CO$_6$) dimethyl-disulfide (DMDS)

As-grown amorphous MoS$_2$ films $\rightarrow$ annealed crystalline

**ALD**

![TEM image of the MoS$_2$ film annealed at 900°C for 5 min](image)

Jin et al. (Konkuk) Nanoscale 6, 14453-14458, 2014.

**MOCVD**

![MoS$_2$ devices on fused silica](image)

![MoS$_2$ devices on SiO$_2$/Si](image)

Courtesy of: Jiwoong Park (Cornell)
K. Kang, S. Xie et al.
Nature (in press)

**Raman shift (cm$^{-1}$)**

- **as-grown**
- **annealed**

200 250 300 350 400 450

2 nm

- **E$_{2g}$**
- **A$_{1g}$**

$\Delta d_{002} = 0.63$ nm
Summary

- **CVD Basics**
  - Precursor Diffusion/ Deposition Kinetics

- **Multi-layer MoS$_2$ Growth**
  - Pressure and Temperature Dependence

- **Single-layer MoS$_2$ Growth**
  - Seeded 1L/ Non-seeded 1L Growth

- **Alternative MoS$_2$/ TMD Growth Methods**
  - ALD, MOCVD
MoS$_2$/ TMD CVD Growth Concluding Remarks

- **Controllable ML MoS$_2$ Growth**
  - Large area, uniform films possible
    - Limited only by size of CVD system
  - Number of layers tunable
    - Solid pressure and temperature control
  - Grain size needs improvement

- **Demonstration 1L MoS$_2$ Growth**
  - Seeded, single crystalline growth consistent
    - Heavy residual contaminants
  - Non-seeded, single crystalline growth possible
    - Inconsistent, not as well controlled

- **Ongoing Challenges/ Improvements**
  - Precursor control/ selection
  - Ordered nucleation control
  - Crystallinity
  - Film uniformity
Wong Research Group
Back Up/ Extras.
Precursor Diffusion/Deposition Kinetics

- Substrate
  - Surface Diffusion
  - Surface Reactions

- Adsorption

- Desorption

- Diffusion

- Reaction

- Forced-Convection Region

- Carrier Gas Reactant Precursor/Gases

- Gas-Phase Processes

- Carrier Gas Reactant Precursor/Gases

- Surface-Phase Processes
Effect of Temperature and Pressure on Deposition Rate

Two Regimes for CVD Growth:

- Fast Surface Reaction
- Mass-Transport Limited Growth
- Slow Surface Reaction
- Surface-Reaction-Rate Limited Growth