Frontiers in MBE Growth of TMDs and Topological Insulators

OR: HOW I LEARNED TO STOP WORRYING AND LOVE THE EVAPORATION OF REFRACTORY METALS

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Outline

- Molecular Beam Epitaxy (MBE)
  - MBE growth of TMD and TI materials
    - Complications
    - Current status of the field
  - Recent results in TI materials
    - Axion insulator
What is Molecular Beam Epitaxy (MBE)?

- One of more streams of atoms are aimed at a substrate
  - Sublimated thermally in ultra high vacuum
- Grow a crystal **one atomic layer at a time**
  - Controllably add impurities to create useful properties
- Use Reflection High Energy Electron Diffraction to monitor growth surface

![Diagram of Molecular Beam Epitaxy](image-url)
MBE with conventional materials

- In-situ monitoring of growth by RHEED
  - Real time observation of growth mode
  - Growth rate by RHEED oscillations
- Layer-by-layer control
  - Atomic period superlattices
- Very clean environment
  - Ultra high vacuum (UHV), >5N purity sources
- Very high mobility 2DEG samples
  - e.g. InAs 2DEG grown on InP substrate
  - Carrier density $6.2 \times 10^{11}$ cm$^{-2}$
  - Mobility > 1,000,000

Volmer-Weber
3D Island
Frank-van der Merwe
Layer-by-layer
Stranski-Krastanov
Mixed

$\Theta<1$ ML
$1<\Theta<2$
$\Theta>2$


Manfra Group
Layered materials, van der Waals bonds between layers.
- Naturally 2D. Scaling down in Z dimension is provided for free
- Spans metals to semiconductors to superconductors
  - Thickness dependent bandgaps
  - Novel spin and optical properties

Topological Insulators
- Large spin orbit coupling
- Spin polarized surface states
2D materials: TMDs and TIs

- **van der Waals epitaxy (VDWE)**
  - Traditional growth models like Stranski-Krastonov may not apply
  - Lattice matching materials isn’t as important
  - Choose materials based on electronic/optical properties not physical lattice properties

**Transition Metal Dichalcogenide**

MoS$_2$

![MoS2 diagram](https://commons.wikimedia.org/w/index.php?curid=2976497)

**Topological Insulator**

$(\text{Bi}_{1-x}\text{Sb}_x)\text{Te}_3$

![Topological Insulator diagram](https://commons.wikimedia.org/w/index.php?curid=2976497)

**TMD on TI**

20% lattice mismatch!

![TMD on TI](https://commons.wikimedia.org/w/index.php?curid=2976497)

*Yue, 2D Mater. 4, 045019 (2017)*
Misses a number of papers, but gives an idea of how MBE VDWE of TMDs is growing.
Differences from conventional MBE

- VDWE – Prone to twins and rotations due to lack of strongly orienting bonds
- Nucleation leads to grain boundaries
- Large state space to optimize within
  - Temperature
    - Diffusion and absorption
    - Higher better for limiting nucleation
  - Growth rate (slow)
  - Flux ratios (typically 20:1, maybe 1000:1)
  - Substrate (graphene, sapphire, CaF\textsubscript{2})
  - Bond energies between constituent atoms
- Theoretical modeling of growth dynamics is very important
10 ML WSe$_2$ on Sapphire

- Recent work from Univ. of Tokyo, RIKEN
  - RT seed layer, annealed at high T
  - Layer-by-layer growth (RHEED oscillations)
  - Then high T post-anneal
- Ambipolar transport with ionic liquid gating
- XRD rocking curve is wide
  - Probably due to domain boundaries

RHEED oscillations

Nakano, NanoLett 17, 5595 (2017)
1 ML MoSe$_2$ on Sapphire

- Cho group at Yonsei, Korea
  - Towards wafer scale fabrication
  - Observe changes in optical adsorption related to changes in bandstructure with film thickness

Interfacial layer?

Island nucleation and coalescing leads to grain boundaries

- Dislocations at small angle grain boundaries
- Can even lead to buckling of the film

**AFM**

$\text{Bi}_2\text{Se}_3$ on InP (111)

**XRD**

$(\text{Bi,Cr,Sb})_2\text{Te}_3$ on InP (111)

**Plan view TEM**

$\text{Bi}_2\text{Se}_3$ on Sapphire

"String of pearls" dislocations

Moiré patterns

G. Smith et al., (in preparation)

APL Mat. 3, 083303 (2015)

https://www.uni-ulm.de/fkp/lehre/gl5/ComKurs1/question/crystal/sol4.htm
Issue: Grain boundaries

- Defects at boundaries limit mobilities
- In some materials like MoSe2, states seen in STM
  - Easy way to see domain sizes in monolayer films
- Can create states in the bandgap

STM of MoSe2 at -1V bias


Hong, NanoLett. 17, 6653 (2017)
Effect of growth temperature

- WSe$_2$ on HOPG (UT, Dallas)
  - Several times larger grain size, but very slow!
  - Similar for MoSe$_2$ (N. Comms. 8, 15135 (2017))

$T_{\text{sub}} = 500^\circ\text{C}$ for 3 hours

Yue, 2D Mater. 4, 045019 (2017)
Nucleation: Surface reactions

- Passivating substrates prior to growth is common
- Defects may dominate nucleation sites
  - Issue for both CVD and MBE

- e.g. Benzaldehyde adsorption on water passivated silicon(001)
  - By STM, 1/(100) Si surface atom is not passivated
    - Dangling bonds are bright spots
  - Benzaldehyde reacts at dangling bonds

2D materials, the surface is the device. Chemical stability is critical.

Surfaces may be stable in air

Edges and domain boundaries are vulnerable to oxidation

- TMDs - Longo et al. 2D Mater. 4 025050
  - Edges become conductive. STM - Addou et al. 2D Mater. 5 025017
- TIs - Similar mechanism
  - Wildly different claims about stability against oxidation because of this

Contacts can have interfacial reactions - Smyth, 2D Mater. 4 025084 (2017)
2DCC: Range of growth strategies

Solid source MBE

Se cracker to increase reactivity
In-Situ characterization

CBE / MOMBE
hybrid MBE

MOCVD
Vacuum suitcase to go between instruments

physical vapor deposition

chemical vapor deposition
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Topological Insulator Surface States

- Large spin-orbit coupling + time reversal symmetry leads to novel topology of bandstructure
- 2D ‘helical Dirac fermions’ on surfaces
  - Bi$_2$Se$_3$, Bi$_2$Te$_3$, Sb$_2$Te$_3$ (and their alloys)
- ‘Spin-momentum locking’ of 2D helical Dirac surface states: spintronic devices.

Fu & Kane, Phys. Rev. B 76, 045302 (2007)
Transport in Topological Insulators

- Want electrons to move only thru surface states
  - Want $E_F$ in bulk bandgap where surface states are
- Break degeneracy of the Dirac point by magnetic doping
  - Massive Dirac Hamiltonian
  - To open a gap, the magnetization must be out of plane
  - Can create a new chiral edge state

$$H(k) = A(\sigma^x k_y - \sigma^y k_x) + \sigma^z m_z$$
$$E = \pm \sqrt{(Ak_x)^2 + (Ak_y)^2 + m_z^2}$$
Half quantum Hall effect on the surface

$\sigma_H = e^2/h$

$J_t = \frac{E_x}{4\pi}$

$J_b = \frac{E_x}{4\pi}$

When parallel, “domain wall” traps a chiral edge state.


Quantum anomalous Hall (QAH) effect

Topological magnetoelectric effect (TME)

- Material showing TME

\[ \theta = \pi \text{ for TI} \]
\[ \theta = 0 \text{ for NI} \]

Axion electrodynamics!
F. Wilczek, PRL 58, 1799 (1987)

Axion insulator:

Criteria:
- 3D regime
- Gapped all surfaces
- Maintain $\theta = \pi$ in the bulk

A theoretical Proposal:

\[
\begin{align*}
S_\theta &= \frac{\theta}{2\pi} \frac{e^2}{h} \int d^3x \, dt \mathbf{E} \cdot \mathbf{B} \\
\theta &= \pi \text{ for TI} \\
\theta &= 0 \text{ for NI}
\end{align*}
\]

Recent reports:


No experimental evidence of “antiparallel”.

Axion Insulator
Axion Insulator

Our version:


Transport measurement setup:
Leiden Cryogenics, 30mK PPMS, ~2K and above

See also:

V-QAH sample

0.15

T

Hc2

Hc1

Cr-QAH sample

\( \rho_v (u_0 H) \)

\( H(T) \)

QAH Insulator
parallel magnetization alignment

Axion Insulator
anti-parallel magnetization alignment

3QL V(9B,9S)_2Te

4,5

4QL 9B(9S)_2Te

3QL Cr(8B,8S)_2Te

SrTiO_3(111)

Sample with Te cap

STO substrate

Indium contacts

Back gate

Sample with Te cap

500 µm

1000 µm

See also:
Signature of an Axion Insulator

3-5-3 sandwich heterostructure SH1

Resulting from the antiparallel magnetization alignment.

Zero $\sigma_{xy}$ plateaus

$-H_{c1} < H < -H_{c2}$

$H_{c2} < H < H_{c1}$

Temperature dependence of Hall resistivity

2-step transition up to 10K.
Evidence of Antiparallel Magnetization

Magnetic Force Microscopy (MFM):

3-5-3 sandwich heterostructure SH2

$\delta f$: RMS of the MFM signal

$\delta f$ (mHz)

$\rho_{\text{int}} (\text{h/e}^2)$

$V_g = 0 \text{V}$

$T = 5.3 \text{K}$

$f = 5 \text{mHz}$

$f = -5 \text{mHz}$

$\mu_0 H (\text{T})$
Gate Dependence

3-5-3 sandwich heterostructure SH1

Crossing valence band, RKKY

OFF/ON ~8000

QAH and axion insulator states persist within the gap.

3/27/2018
Conclusion

- Challenges of MBE of van der Waals materials
  - Current state of the field with MBE of TMD and TI materials
  - Domain sizes and boundaries

- 2DCC capabilities
  - Growth and in-situ characterization

- Recent axion insulator results with magnetic tri-layer TIs
  - Successful growth of Cr- and V- doped QAH sandwich heterostructures.
  - Low temperature transport and MFM data demonstrate the axion insulator state with antiparallel magnetization alignment.
  - Observation of the axion insulator paves the way to explore the TME effect and other fascinating topological phenomena.

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