Hybrid growth approaches and hybrid materials options: Unconventional opportunities available in 2DCC-MIP

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Chalcogenide-based crystals
- large variety of crystal structures
- host diverse chemistries
- structures highly anisotropic

Access to interesting band structures providing intriguing features that are beyond the conventional semiconductor materials
- superconductors
- topological insulators
- piezoresistive materials

Can be tuned through various materials design degrees of freedom
- dimensionality
- layering schemes
- intercalation
- proximity to other functional materials through monolithic integration

Transformative new science to be discovered that enables next generation Electronics.
Elemental landscape as MBE grower:

- Expanding growth horizon from oxides ‘down the Group VI column’
- Dramatic differences in vapor pressure of different constituents for TM compounds: FeSe vs. NbSe$_2$
- Layered structure open structure: high diffusivity
- Rocksalt structure of monochalcogenides: prone to accommodate defects
2D Crystal Consortium Platform

Develop custom deposition tools with *in situ* and real-time characterization of monolayer and few-layer films.

Unique capabilities in simulation of reaction kinetics through first principles + reactive potential approach.

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**2D MATERIALS**

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

**In-situ Characterization**

**Hybrid MBE**

- **Chalcogenide MOCVD**
- **Bulk Growth**

**Synthesis**

**Theory/Simulation**

- **DFT**
- **Monte Carlo**
- **Molecular Dynamics**
- **Reactive Force Field**
- **Phase Field**

Closed Development Loop
Outline of the talk

- Hybrid growth approaches: combining molecular beam epitaxy and chemical vapor deposition in one reactor for the growth of 2D layered materials

- Lessons learned and challenges ahead: the role of substrates, film nucleation and formation of chalcogenide vacancies

- Overcoming synthesis challenges using theory-synthesis-team approach: the role of surface chemistry on nucleation behavior (collaboration with A. van Duin: Al$_2$O$_3$ on Ge(001))

- Monolithic integration of chalcogenides with oxides: opportunities from in-vacuo connection with hybrid MBE growth reactor
Wide range of growth strategies utilizing low energy deposition techniques

Solid source MBE

Samarth Webinar 8-30-16

hybrid MBE

physical vapor deposition

MOCVD

chemical vapor deposition

Redwing Webinar 9-27-16

https://www.mri.psu.edu/materials-innovation-platform/webinars
Hybrid MBE for chalcogenides

- conventional MBE reactor (background pressure $10^{-10}$ Torr)
- multiple effusion cell ports and RF plasma source (substrate surface clean/conditioning)
- e-beam evaporator with extra long throw distance minimal thermal load on the sample, easier flux control
- capability to load up to 3’ wafer
- special sample holder to directly grow on substrates mounted on a T-Omicron holder
- Cluster flange with multiple gas injector lines to supply high vapor metalorganic precursor
- Individual sections gate-valve isolated for max. up-time

System designed for high throughput, short down time, max. flexibility.
Hybrid MBE for chalcogenides

- in-situ RHEED
- in-situ Spectroscopic Ellipsometry (precise temperature monitoring, adsorption, desorption, diffusion)
- fully automated flux calibration procedure
- beam flux monitor & heated quadrupole mass spectrometer
Hybrid MBE approach for TM chalcogenides

- **Challenge:**
  - high thermal load when supplying low vapor pressure transition metals
  - MBE low pressure: high volatility of chalcogen: vacancy formation
  - lowering growth temperature limits surface diffusivity
MBE of transition metal dichalcogenides: status of field

• only few reports on selected TMDs (MoTe$_2$, MoSe$_2$, WSe$_2$, HfSe$_2$)
• Grain sizes seem to be very small (< 100 nm)
• Unfavorable combination of surface diffusivity of TM element vs. volatility of chalcogenide and bulk diffusion

Need to supply TM element in more volatile form prone to high diffusivity
Hybrid MBE approach for TM chalcogenides

- Many precursors available
- Low temperature supply ~100 °C, no carrier gas needed
- Decomposition of pure element and precursor with chalcogenides available

Advancements in the development of new metalorganic anticipated
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Towards ‘electronic grade’ Chalcogenides

High carrier density
[3-4 × 10^{13}/cm^2, need <1 × 10^{13}/cm^2]

Low surface mobility
[500 cm^2/Vs]

Two options: (1) Compensation doping and (2) better substrate

Option 1: Compensation doping with Cu

- Compensation doping successful
- Lowering sheet carrier concentration by about 1 order of magnitude
- Pronounced increase in mobility
- Larger Cu concentration: Cu at interlayer interstitial acts as donor

\[ \text{Cu}_x \text{Bi}_2 \text{Se}_3 \]

\[ x_c \sim 3\% \text{Cu}_{0.03} \text{Bi}_2 \text{Se}_3 \]


Layered structure poses challenge to keep dopants in the right lattice sites.
**Option 2: Better substrate match**

- **Al₂O₃**: 14% lattice mismatch, chemically inert
- **InP**: 0.2% lattice mismatch, covalent bond, reactive: textured surfaces, twins, small grain sizes ~200 nm
- **In₂Se₃**: 0.2% lattice mismatch, band insulator, NO surface states, van der Waals gap, weak bonding (inert)

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**bulk In₂Se₃ does not exist**: templated growth approach
Option 2: Better substrate match

- nucleate 3QL Bi$_2$Se$_3$
- grow metamorphic layer 20 QL In$_2$Se$_3$
- challenge: Defective layer will short the pristine layer

Koirala et al., Nano Lett. 15, 8245 (2015)
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- nucleate 3QL Bi$_2$Se$_3$
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- growth on template layer: In diffuses into Bi$_2$Se$_3$ suppressing topological properties (3-7%)
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- grow metamorphic layer 20 QL In$_2$Se$_3$
- challenge: Defective layer will short the pristine layer
- heating layered structure to drive out buried defective Bi$_2$Se$_3$ layer
- growth on template layer: In diffuses into Bi$_2$Se$_3$ suppressing topological properties
- incorporation of an insulating (Bi$_{0.5}$In$_{0.5}$)$_2$Se$_3$ buffer layer as diffusion barrier

Koirala et al., Nano Lett. 15, 8245 (2015)
Option 2: Better substrate match

\[ n_{2d} \sim 2.0 \times 10^{12} \text{ cm}^{-2} \]
\[ \mu \sim 16,000 \text{ cm}^2/\text{Vs} \]

Lowest defect density!

Record mobility!

Observation of integer quantum Hall effect

Film nucleation, growth, bulk diffusion and must be precisely controlled
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In-situ Spectroscopic Ellipsometry & ReaxFF

**In-situ Spectroscopic Ellipsometry (SE)**
- Provides real-time feedback of surface optical properties
- Highly surface sensitive at atomic scale
- Provides thin film thickness, optical constants, etc

**Reactive Force Field (ReaxFF) Simulation**
- Empirical force field optimized against quantum mechanics
- Large simulation scales & low cost
- Describes reactive events at interfaces between solid, liquid, and gas
**In-situ Spectroscopic Ellipsometry: baseline**

- Coalesced ALD is linear growth
- TMA dose → Nominal thickness increase  
  → Increase amplitude = TMA adsorption level
- H₂O dose → Nominal thickness decrease
- GPC/TMA-adsorption ratio is constant for a simple reaction of TMA+H₂O → Al₂O₃
ReaxFF: nucleation delay of $\text{Al}_2\text{O}_3$ ALD on Ge:H

- High reaction barrier limits TMA chemisorption on Ge:H

- High reaction barrier limits H2O chemisorption on Ge:H

- Endothermic $\rightarrow$ Hydrophobic Ge:H
ReaxFF: nucleation delay of Al$_2$O$_3$ ALD on Ge:H

ReaxFF Simulations

- Local dangling bond sites (Ge-*') can form at elevated temperatures
- TMA energetically favors Ge-*' sites
  - Ge-Al formation
- Catalyzes H dissociation at neighboring Ge-H site
- Ge-*' serves as a highly localized nucleation center
Al₂O₃ ALD nucleation on GeOₓ(5Å)/Ge(100)

- **Region-I**
  - Strong TMA adsorption + High GPC
- **Region-II**
  - Moderate TMA adsorption + Very low GPC
- **Region-III**
  - Transition to coalescence
- **Region-IV**
  - Coalesced Al₂O₃ ALD
- **GPC/TMA-adsorption deviates from baseline in Region I-III**
  → Not a simple TMA+H₂O reaction!
ReaxFF: Al$_2$O$_3$ ALD nucleation on GeO$_x$(5Å)/Ge(100)

ReaxFF Simulations

- **1$^{st}$ TMA dose:** strong TMA chemisorption
- **2$^{nd}$ TMA dose:**
  - less TMA adsorption
  - Al atoms diffuse into GeO$_x$ layer and intermix
- H$_2$O dose removes residual -CH$_3$ groups
- Ge+4 reduced by TMA → Self-cleaning
- Oxygen in Al$_2$O$_3$ mainly from GeO$_x$

Successful identification of reactive processes at play during film nucleation using ReaxFF, can be expanded to the growth of chalcogenide films
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MBE #1: Existing Growth Capabilities

Multiple *in vacuo* transfer options to broaden the user community and ensure full compatibility of growth and characterization capabilities.
Combination of promising chalcogenide films with functional oxides gives rise to intriguing phenomena

1. Phonon coupling between the oxide and chalcogenide$^{1,2}$
2. Chemistry at the interface IE TiO$_2$-FeSe mixing and doping$^3$
3. Structure: Strain, atomic reconstructions, etc...

Epitaxial integration of Chalcogenides on Oxides


AFD transition in SrTiO$_3$

Compressive strain = -1.26 % for SrTiO$_3$ on LSAT substrate

SHG reveals both FE and AFD transitions at higher temperature

$T_{\text{sub}} = 900 \, ^\circ\text{C}$

$P_{O_2} \sim 1 \times 10^{-7} \, \text{Torr}$

$\Phi_{\text{Sr}} = 3.0 \times 10^{13} \, \text{atoms/cm}^2/\text{s}$

Summary

• Hybrid growth approaches: combining molecular beam epitaxy and chemical vapor deposition in one reactor
  – advantages for growth of refractory metal chalcogenides
  – in-situ growth metrologies allowing to study non-equilibrium processes during growth
  – provides excellent handle to minimize undesired effects (e.g. bulk diffusion)
  – enhance sample-to-sample reproducibility

• Lessons learned and challenges ahead:
  – correct substrate key
  – development of diffusion barrier growth template of tremendous importance

• Overcoming synthesis challenges using theory-synthesis-team approach: the role of surface chemistry on nucleation behavior
  – Combined theory-experimental approach to quickly improve synthesis strategies
  – rigorous treatment of complex kinetic processes at surfaces demonstrated, can be readily expanded to chalcogenide systems

• Monolithic integration of chalcogenides with oxides:
  – opportunities from in-vacuo connection with hybrid MBE growth reactor
  – Complex bottom functional structures (e.g. ferroelectric, antiferromagnetic, superconductor) possible