Chalcogenide Semiconductor Nanostructures

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__Labs__: Photoemission -- PAB B049 (Olmstead Lab)
Scanning Probe Microscopy -- PAB B009 (Fain Lab)
High-resolution Photoemission -- Advanced Light Source, Berkeley

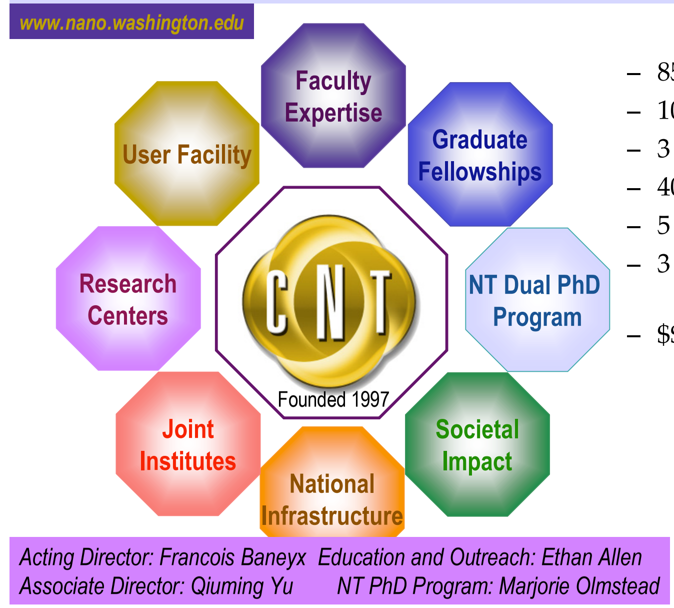
__**Funded Projects:**__

- Intrinsic Vacancy Chalcogenides for Spintronic Applications
- Phase Change Materials for Nanoelectronics:
  A combinatorial approach to mechanistic understanding

__**Part 1: Nanotechnology Ph.D. Program**__

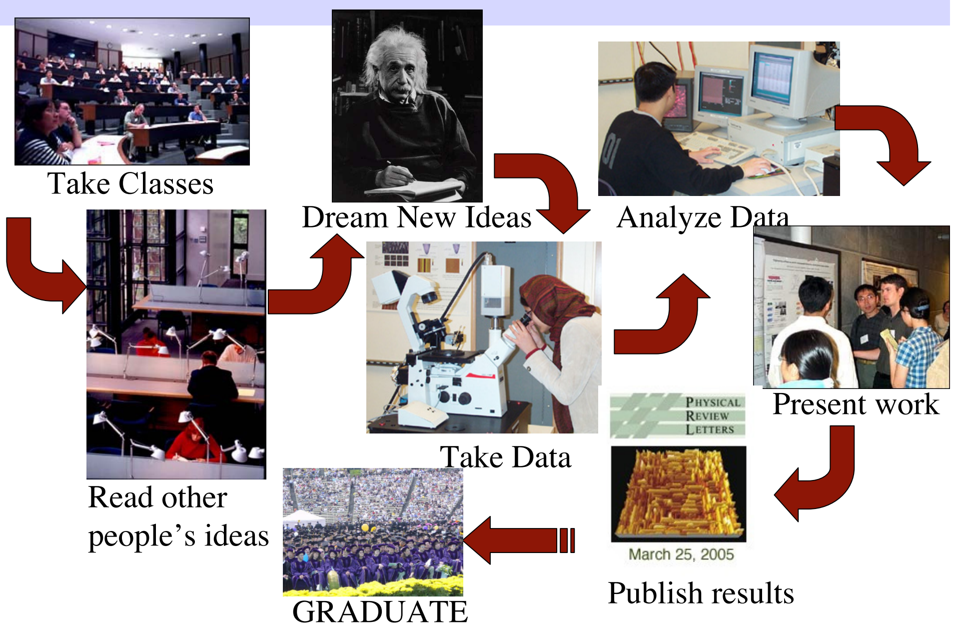
__**Part 2: Research in Olmstead and Fain Groups**__

UW Center for Nanotechnology



- 85 Faculty
- 10 Departments
- 3 Colleges
- 40 PhD Students
- 5 Centers
- 3 International Partnerships
- $$ UW, NSF, NIH, DOE, Non-Federal

"Standard" Ph.D. Process

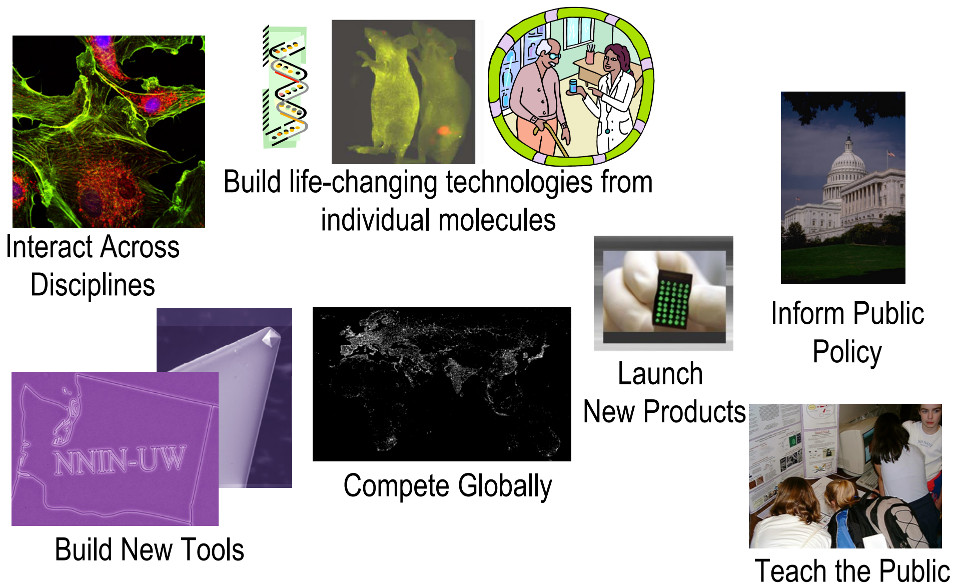


"Standard" Ph.D. › "Standard Job"

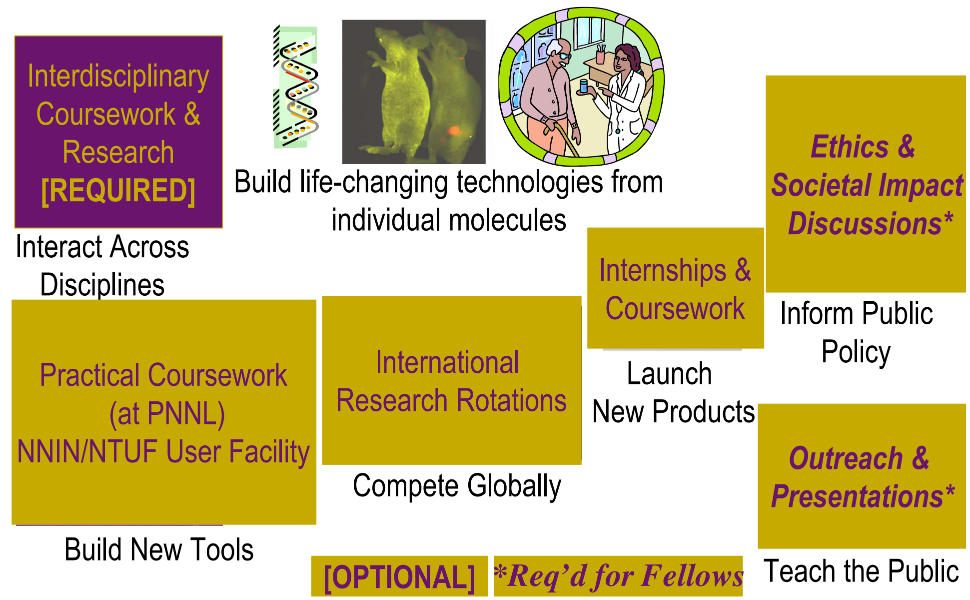
- Basic Research
- Perhaps Teaching
  (though often not part of training)
- Everything else gets learned on the job



What Do Nanotechnologists Do?



New Educational Strategies: IGERT NSF/NCI Graduate Training Program



Dual Degree in Nanotechnology

1. Thesis in Nanoscale Science or Technology
   - Approved in quality by home department
   - Approved as "nano-relevant" by NT Standards Committee
   - Advisor + at least one other committee member in the Center for Nanotechnology
2. Core course *Frontiers of Nanotechnology*
   - Student joint projects across disciplines
   - Discuss societal impact as well as science & technology
3. Research Rotation
   - ≥ 1 quarter research *outside* advisor's home department
4. Nano-relevant Course Work
   - ≥ 3 courses, ≥ 2 of which are *outside* home department
5. Nanotechnology Seminar
   - Attend ≥ 80% of seminars, ≥ 4 quarters

"Optional" Essentials

- Communication amongst disparate groups
  - Nanoscience & Nanotechnology Student Association
  - Student-Run Seminar Series
  - Annual Workshop
  - Quarterly Symposia with Brief Presentations and Longer Social Hour (was Wednesday)
- Outreach and Recruitment for Diversity
  - Individual PLUS Coordinated Efforts
- Career Planning
  - Mentorship and Internship Programs
  - Bring Non-academics to Campus
- Fellowship Program
  - Proposal writing experience
  - Bias toward Interdisciplinary Collaborations
  - IGERT, UIF, hopefully more.
- User Facility
  - Students are Trained Users AND become "Trainers" of Others

Path to a UW Nanotechnology Ph.D.

University of Washington
Incoming Graduate Students

Admission into a "Home" Department

Arts&Sciences: Phys & Chem
Engineering: BioE, ChemE, EE, Mat. Sci.
Medical School: Biochem, BioE, Genome Science, Physiol&Biophys

Fulfillment of all Doctoral Requirements of Home Department

Optional Degree Program in "Nanotechnology"

Requirements:
Laboratory Rotations
Interdisciplinary Course Work
Research Thesis in Nanoscale Science and/or Nanotechnology
Frontiers in Nanotechnology
Nanotechnology Seminar

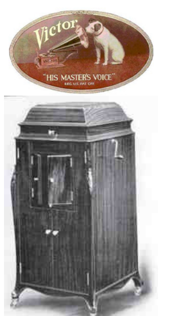
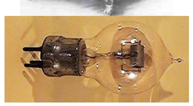
Options:
Competition for Graduate Student Awards in Nanotechnology (funded by NSF-IGERT and the UW)
Hands-on Training and Research in the NanoTech User Facility
Membership in Nanotech Student Association
Mentoring Program
Industrial Internship and Research at PNNL

Graduation with "Ph.D. in 'Home Department' and Nanotechnology"

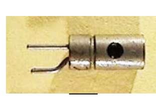
Part 2: Olmstead & Fain Group Research

Nanostructures of Dissimilar Materials

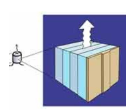
Miniaturization

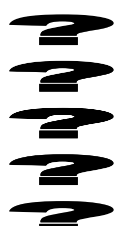
1930's
Victrola


Vacuum Tube
L ~ 1 cm
(10^7 nm)

1960's
Tabletop Turntable


Transistor
L ~ $10^{-3.5}$ cm
($10^{3.5}$ nm)

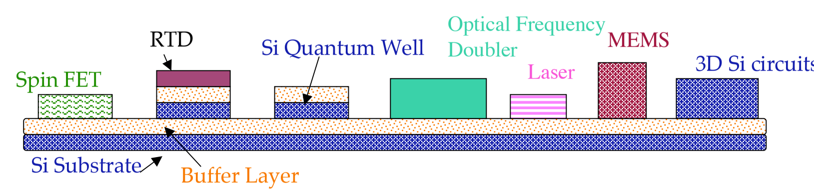
1990's
Walkman


Heterostructure Laser
L ~ 10^{-7} cm
(1 nm)

2020's


Silicon-based Nanoelectronics

Spintronics and Optoelectronics + Miniaturized Si Microelectronics

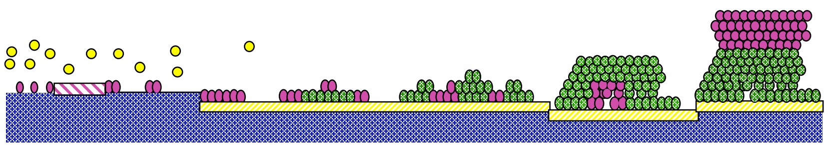


- Need Silicon-Compatible Materials for:
  - Ferromagnetic Injectors — $Co_xTi_{1-x}O_2$; $TM:Ga_2Se_3$
  - Non-linear/polarization dependent optics — Ga_xSe_y and Al_xSe_y
  - Light emission — CaF_2-Si-CaF_2
  - High-k dielectric gates — TiO_2; $Al_2Se_xO_y$
  - Non-volatile Memory — In_xSe_z, Ge-Sb-Te

Requires Atomically Controlled Interfaces Between Dissimilar Materials

Nanoscale Action ⇒ Macroscopic Results

- Factors We Can Control --
  - Temperature — Flux
  - Surface Composition — Average Step Spacing
- Factors We Must Deal With --
  - **Strain** (lattice mismatch)
  - **Surface Structure** (steps, defects, symmetry)
  - **Chemical Reactions** (interface compounds)
  - **Surface Energetics** (diffusion, surface energy)



First Monolayer Controls Subsequent Growth

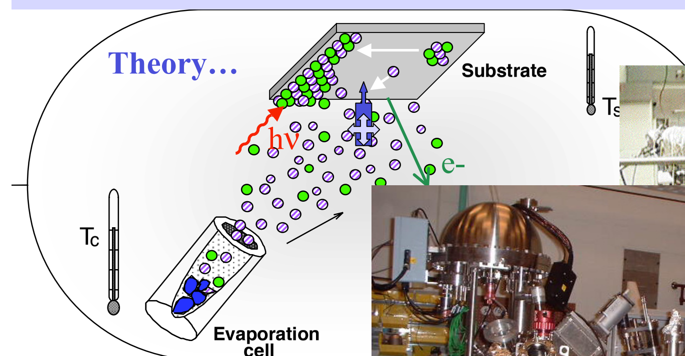
Common Themes in our Research

- Quantify Correlations between Thermodynamics, Kinetics and Nanostructure Properties
- Develop New Materials and Methods to Fabricate Si-compatible Quantum Nanostructures
- Establish a Unifying Predictive Framework for Heteroepitaxy of Dissimilar Materials
- Investigate Physics Underlying Nanoscale Characterization Techniques

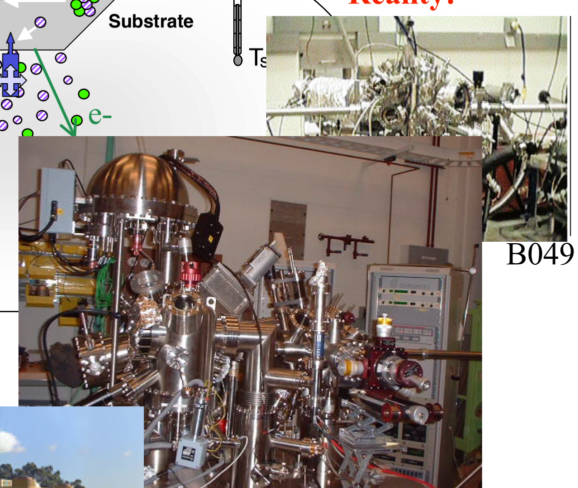
Experimental Probes

Technique	Information
• High Resolution Microscopy – Scanning Tunneling – Atomic Force – Magnetic Force	• Nanoscale Structure
• Low Energy Electron Diffraction • Xray Diffraction	• Average Atomic Structure
• Photoemission Spectroscopy	• Chemical Environments
• Photoelectron Diffraction – Scanned Energy & Angle – Component-Resolved	• Local Structure – Bond Lengths/Angles – Symmetry
• Valence Band Spectroscopy – Scanned Energy & Angle	• Electronic State Density – Surface/Bulk
• Ion Scattering Spectroscopy	• Surface Elemental Composition
• SQuID Magnetometry	• Magnetic Properties

How it's done …

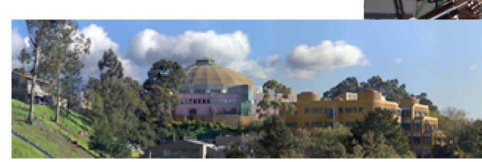


Reality:



B049

B009



ALS-Berkeley

Recent Fain Group Publications

- S. C. Fain, Jr., C. A. Polwarth, S. L. Tait, C. T. Campbell, and R. H. French, **"Simulated measurement of small metal clusters by frequency-modulation non-contact atomic force microscopy (ncAFM) "** Nanotechnology 17, S121 (2006).
- J. M. K. Donev, Q. Yu, B. R. Long, R. K. Bollinger, and S. C. Fain, Jr., **"Non-Contact Atomic Force Microscopy Studies of Ultra-Thin Films of Amorphous Solid Water Deposited on Au(111),"** J. Chem. Phys. 123, 044706 (2005).
- S. L. Tait, L. T. Ngo, Q. Yu, S. C. Fain, Jr., and C. T. Campbell,**"Growth and Sintering of Pd Clusters on α-Al2O3(0001),** "J. Chem. Phys. 122, 064712 (2005).
- B. Pittenger, S.C. Fain, Jr., M.J. Cochran, J. M. K. Donev, B.E. Robertson, A. Szuchmacher, R.M. Overney, "**Premelting at ice-solid interfaces studied via velocity dependent indentation with force microscope tips**," Phys Rev B 63, 134102 (1 April 2001)
- S. C. Fain, Jr., K. A. Barry, M. G. Bush, B. Pittenger, and R. N. Louie, "**Measuring Average Tip-sample Forces in Intermittent-contact (Tapping) Force Microscopy in Air**," Appl. Phys. Lett. 76, 930-932 (14 Feb 2000).
- See http://faculty.washington.edu/fain

Recent Olmstead Group Publications

- **Heteroepitaxial Growth of the Intrinsic Vacancy Semiconductor Al2Se3 on Si(111): Initial Structure and Morphology**, submitted to Physical Review B.
- **Laser and Electrical Current Induced Phase Transformation of In2Se3: Semiconductor Thin Film on Si(111),** Applied Physics A to be published.
- **Semiconducting chalcogenide buffer layer for oxide heteroepitaxy on Si(001),** Applied Physics Letters 88 181903 (2006.
- **Perovskite termination influence in oxide heteroepitaxy**, Journal of Applied Physics 99 113521 (2006).
- **Contrast in scanning probe microscopy images of ultra-thin insulator films**, Applied Physics Letters, 88 063107 (2006).
- **Electronic structure evolution during the growth of ultra-thin insulator films on semiconductors: from interface formation to bulk-like CaF2/Si(111) films**, Physical Review B 72, 204336 (2005).
- **Chemical passivity of III-VI bilayer terminated Si(111**), Applied Physics Letters 87, 171906/1-3 (2005).
- **Intrinsic vacancy induced nanoscale wire structure in heteroepitaxial Ga2Se3/Si(001**), Physical Review Letters, 94, 116102 (2005) Cover photo of March 25, 2005 Issue.
- **Atomically resolved imaging of a CaF bilayer on Si(111): subsurface atoms and the image contrast in scanning force microscopy**, Phys. Rev. B 69, 34505 (2004).
- *COPIES: http://faculty.washington.edu/olmstd*

Example: Silicon-based Spintronics

Utilization of electron spin in electronic devices.

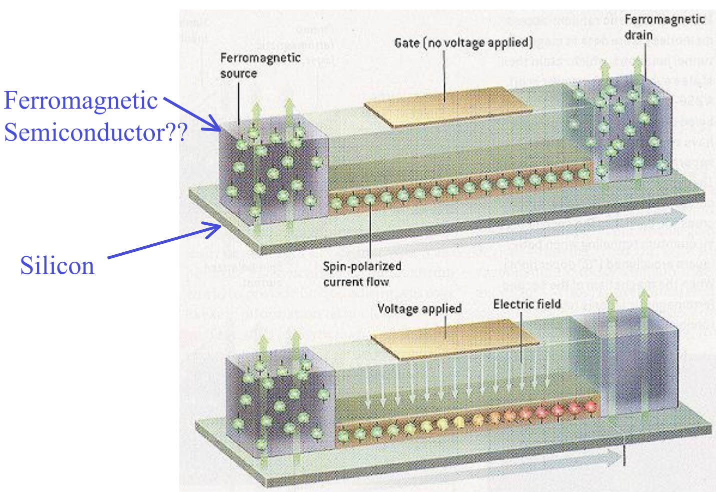
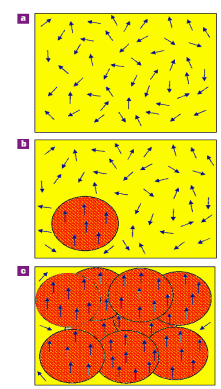


figure credit: Awschalom, Flatte and Samarth, Scientific American, June 2002, p. 67-73

Possible Solution: DMS

- Dilute Magnetic Semiconductor
  - Conductance comparable to silicon channel
  - Use variable electron density to control magnetism
- TM dopants add spin
- Couple spins with free carriers



What material?

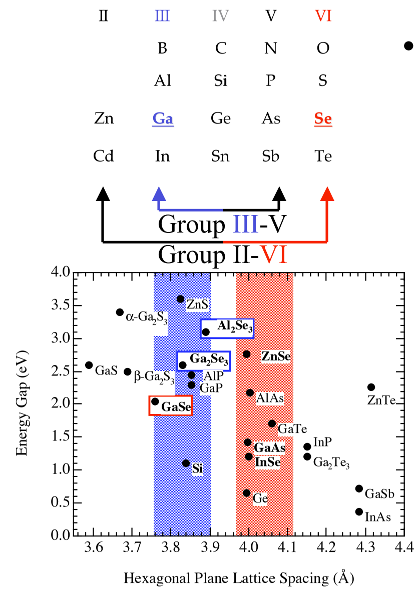
- Device Requirements
  - Ferromagnetic above room temperature
  - Efficient, spin-preserving transport into silicon
- Translation to Materials Requirements
  - Lattice matched to silicon
  - Impedance matched -- Semiconductor
  - Large exchange interaction

Candidate Materials:

Transition Metal Doped Semiconductors

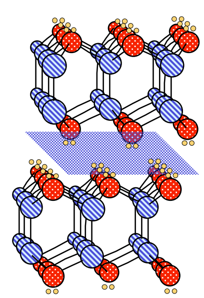
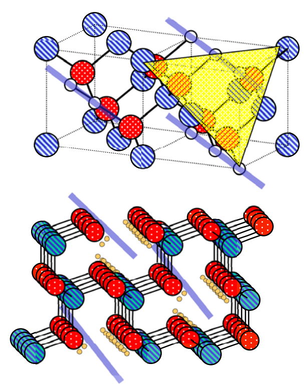
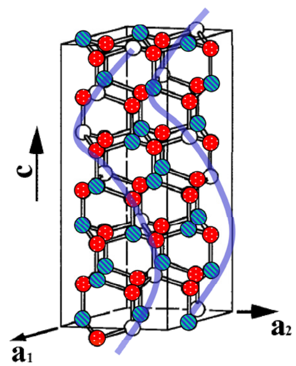
- Mn in GaAs: FM, but only below ~ 100K
- Co or Cr in TiO_2: Thin films ferromagnetic at RT
- Mn or Cr in Ga_2Se_3: New material we propose

Si-compatible III-VI Semiconductors



- **Al_xSe_y , Ga_xSe_y or In_xSe_y = Conventional Semiconductor + e-**
  - Wide band gap semiconductor
  - Lattice matched with Si
  - Extra electron leads to:
    - Vacancies plus sp^3 bonding
    - Structural variety
    - Multiple dopant sites
    - Non-linear optical properties
    - Unique growth morphologies

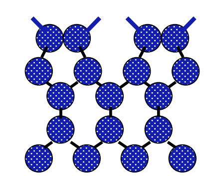
III-VI Semiconductor Crystal Structure

Hexagonal GaSe Layered	Cubic Ga_2Se_3 Zincblende	Hexagonal Al_2Se_3 or In_2Se_3 Wurtzite
		
Planes	Lines	Helices

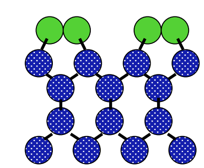
Flexible Bonding Configuration: Vacancies and Lone Pairs

Cubic Substrate: Si(001)

- GaSe on pristine Si(001) 2x1
  - Se-Si Reaction
  - Amorphous Layer
    - No LEED Pattern
    - No Photoelectron Diffraction Structure
- GaSe on As-terminated Si(001) 2x1
  - As Remains at Interface
  - Crystalline Ga_xSe_y
    - 2x1 LEED Pattern
    - Strong Photoelectron Diffraction



Reactive Dangling Bonds

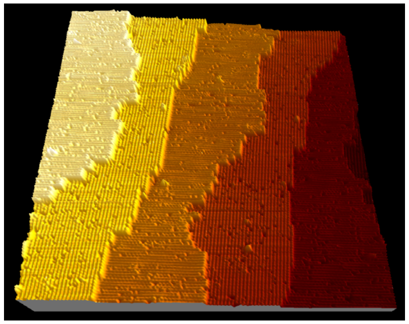


Passivated Reconstruction
Reactive when Open Dimers

S. Meng Thesis (UW) 2000.

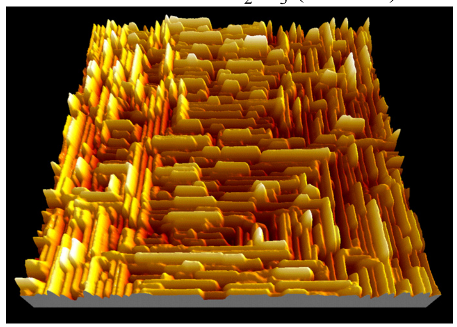
Ga_xSe_y Growth on Si(001)

bare Si(100)



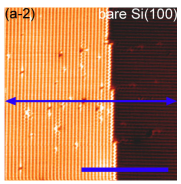
$100x100nm^2$, -2V, 0.1nA

Zinc-blende Ga_2Se_3 (2.5CBL)

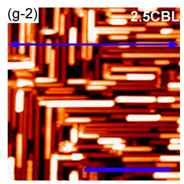


$100x100nm^2$, 5.4V, 0.09nA

Dimer Rows



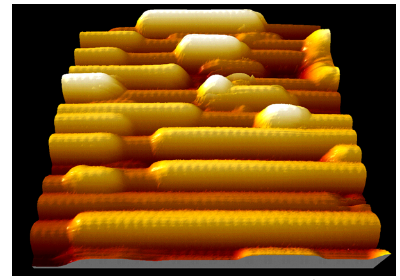
Scale bar 25 nm



Nanorods

T. Ohta et al, PRL 2005.

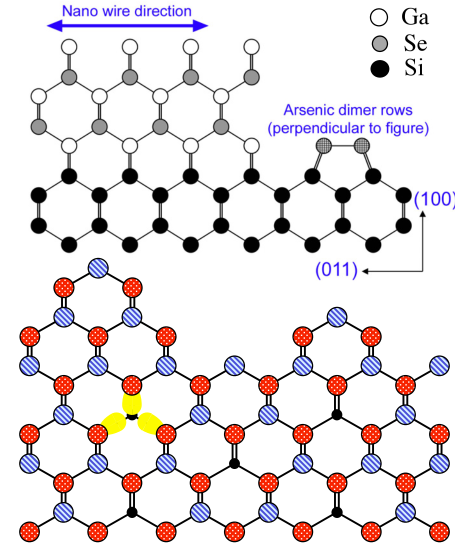
Ga_2Se_3 Nanoridge Structure ⇒ Growth



-5.4 V, 0.09 nA, $20x20nm^2$

- 1 Ga-Se bilayer high
- Corrugation = Ga-Ga distance
- Rods ⊥ to As dimer rows
- Lateral shift between layers

T. Ohta et al, PRL 2005.

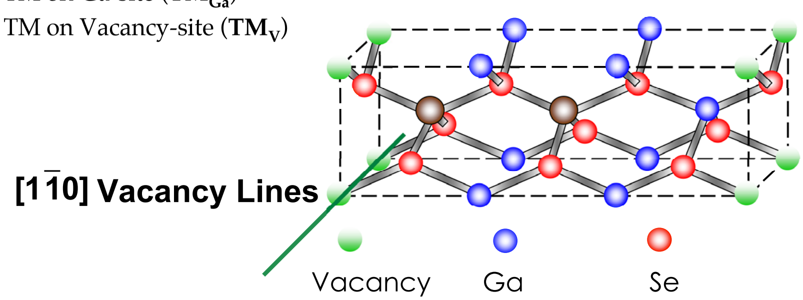


Current Research Direction: Dope Ga_2Se_3

Zn	Ga	Ge	As	Se

$Ge_6 \Leftrightarrow Ga_3As_3 \Leftrightarrow Zn_3Se_3 \Leftrightarrow Ga_2Se_3$

- Zincblende, with Ordered Vacancies
- E_g ~ 2.3 eV
- Lattice Matched to Si (*0.1% mismatch*)
- Two cation sites available for TM doping
  - TM on Ga-site (**TM_{Ga}**)
  - TM on Vacancy-site (**TM_V**)



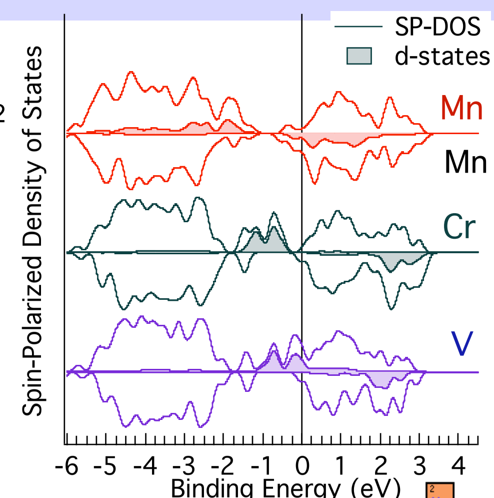
Theoretical Prediction

TM_V

$TMGa_8Se_{12}$

+ = spin ↑

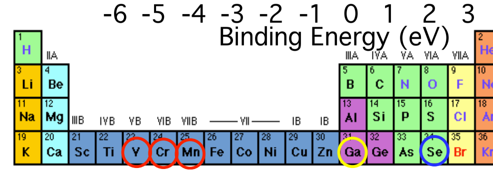
– = spin ↓



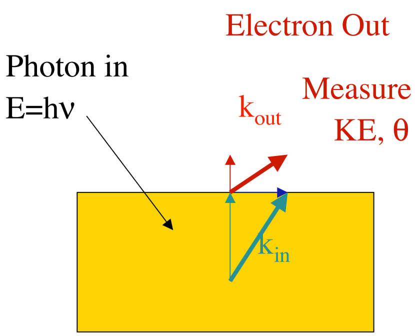
Mn gap ~ Ga_2Se_3 gap

Cr states fill Ga_2Se_3 gap

V states fill Ga_2Se_3 gap and overlap CB



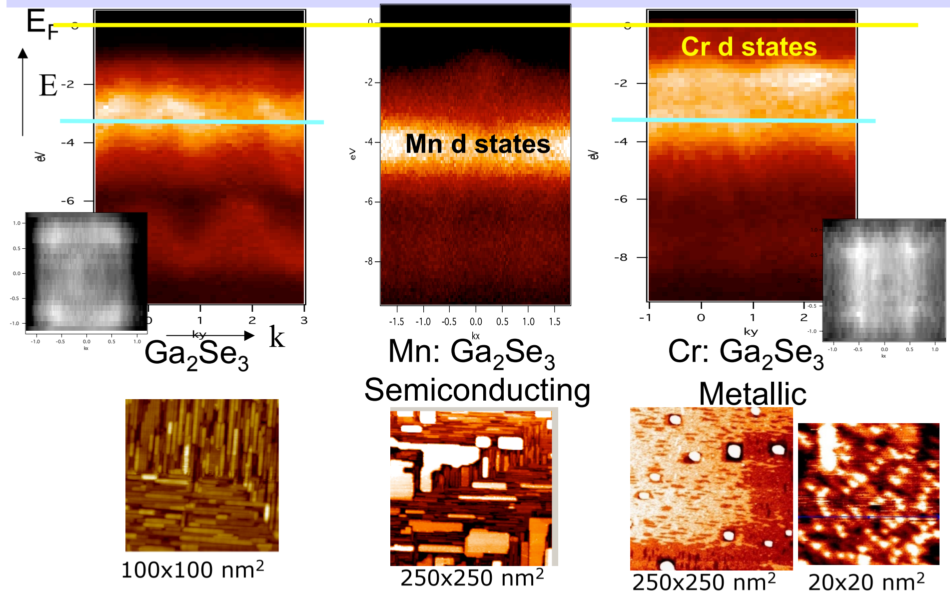
Angle-Resolved Photoemission



Determine E(k) inside crystal

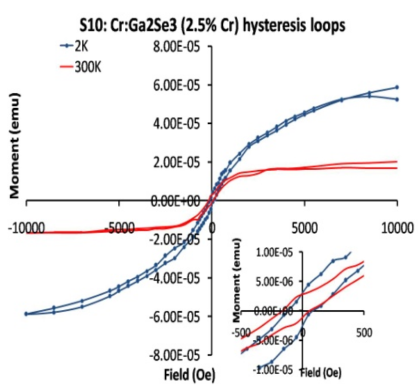
Experimental Bands

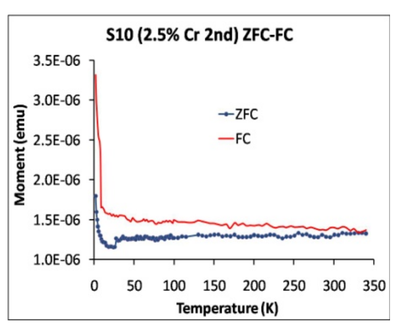
Data from ALS



Cr-doped = Magnetic

- Ferromagnetism at both 2K and 300 K
  - Hysteresis loop
- Apparent Curie Temperature 335 K





Phase Change Chalcogenides

- Amorphous – Crystalline Phases
  - Different reflectivity
  - Different resistivity
- $Ge_2Sb_2Te_5$ (GST)
  - used in commercial DVD, CD-RW
  - 20% cation sites = vacancy
- Challenges
  - Smaller bit size
  - Controlled nucleation
  - Uniform Stoichiometry

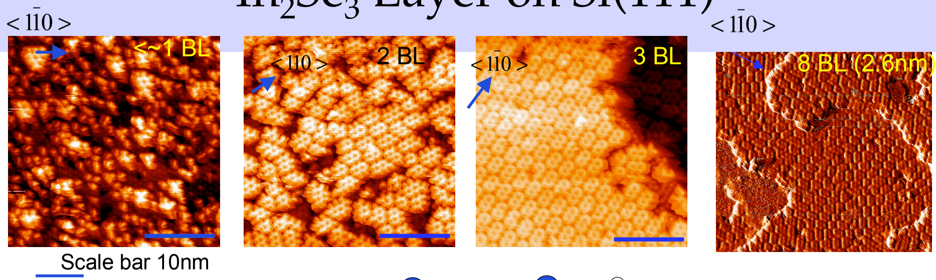
Collaborations:

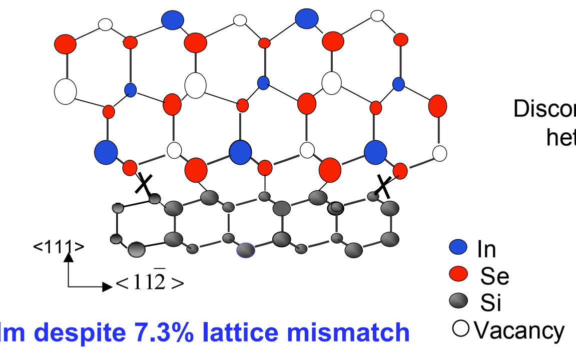
PNNL, Richland

Micron, Boise

NIMS, Japan

In_2Se_3 Layer on Si(111)



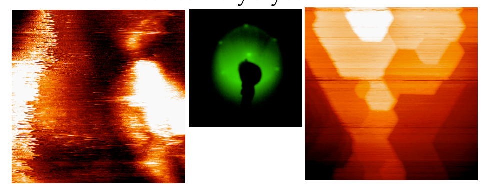


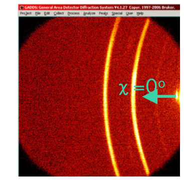
Discommensurate heterointerface

Laminar film despite 7.3% lattice mismatch
Indicating the heterointerface is discommensurate

In_2Se_3 Phase Change

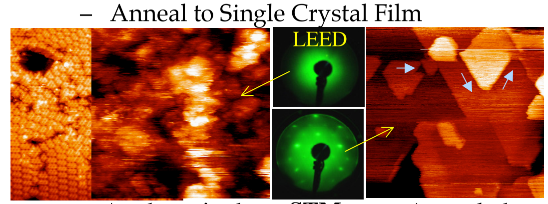
- Room Temperature Deposit
  - Anneal to Polycrystalline Film



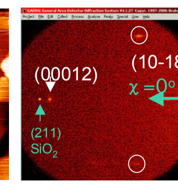


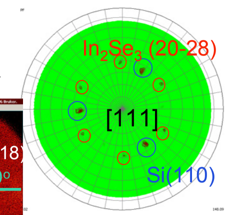
X-ray Diffraction

- Deposit 2 BL at High Temperature
- Add Room Temperature Deposit
  - Anneal to Single Crystal Film



As-deposited Amorphous | **STM: 200x200 nm²** | Annealed to 380°C





Xray Pole Figure

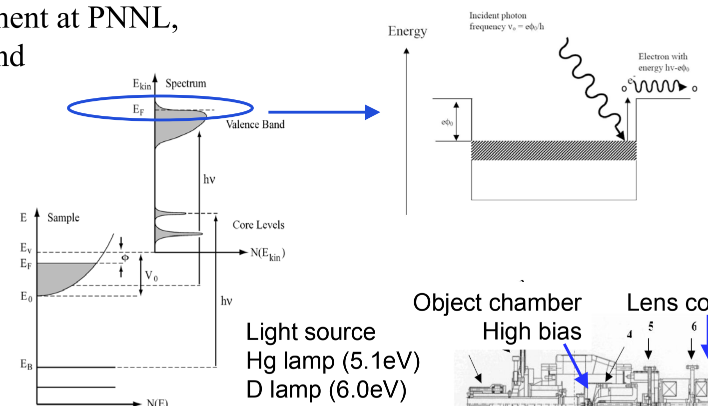
Reverse phase change

Amorphous ⟶ Crystalline : resistive annealing
0 → 1

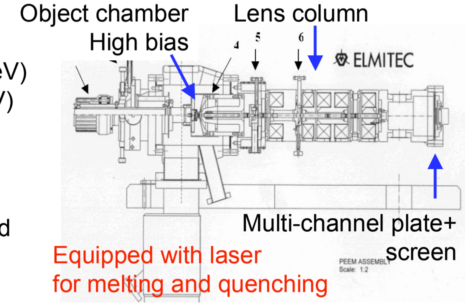
Crystalline ⟶ Amorphous: melting and quenching
1 → 0

Photo Electron Emission Microscopy (PEEM)

Instrument at PNNL, Richland



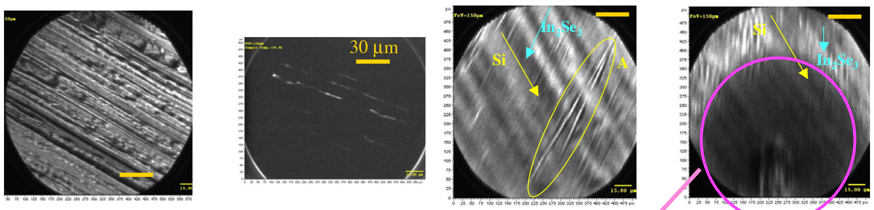
Light source
Hg lamp (5.1eV)
D lamp (6.0eV)



❖Microscopy: real space information.
_ Image contrast often reflects surface chemical composition, phase, and surface dipole.

Reverse phase change: PEEM with laser

Hg lamp, 5.1eV



Clean Si(111) | Amorphous In_2Se_3 | γ-In_2Se_3 | Re-amorphized In_2Se_3

Dark image by using both D lamp and He lamp

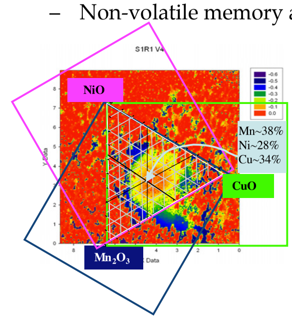
Laser Spot

Reverse phase change

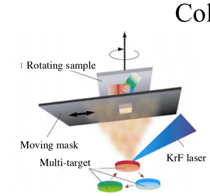
PES: work function change is 0.39eV during phase transformation
Amorphous phase has many electron traps giving dark images

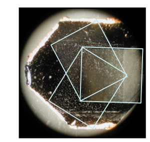
Future Directions

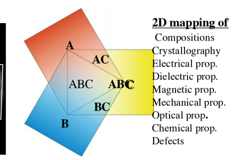
- Spintronics: Study role of TM impurities
  - Growth kinetics and morphology
  - Electronic structure
  - Magnetic properties (MFM shared with MSE)
- Nanostructure Phase Change Memory
  - Role of via in controlling phase stability and uniformity
  - Role of size in controlling energy budget and phase transformation
- Combinatorial Materials -- Novel selenide materials
  - Explore alloy and processing space for new materials
  - Non-volatile memory applications



Collaboration with Micron (Boise)







Chalcogenide Semiconductor Nanostructures

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Labs: Photoemission -- PAB B049 (Olmstead Lab)
Scanning Probe Microscopy -- PAB B009 (Fain Lab)
High-resolution Photoemission -- Advanced Light Source, Berkeley

Funded Projects:

- Intrinsic Vacancy Chalcogenides for Spintronic Applications
- Phase Change Materials for Nanoelectronics:
  A combinatorial approach to mechanistic understanding

Part 1: Nanotechnology Ph.D. Program

Part 2: Research in Olmstead and Fain Groups

Path to a UW Nanotechnology Ph.D.

University of Washington
Incoming Graduate Students

Admission into a "Home" Department

Arts&Sciences: Phys & Chem
Engineering: BioE, ChemE, EE, Mat. Sci.
Medical School: Biochem, BioE, Genome Science, Physiol&Biophys

Fulfillment of all Doctoral Requirements of Home Department

Optional Degree Program in "Nanotechnology"

Requirements:
Laboratory Rotations
Interdisciplinary Course Work
Research Thesis in Nanoscale Science and/or Nanotechnology
Frontiers in Nanotechnology
Nanotechnology Seminar

Options:
Competition for Graduate Student Awards in Nanotechnology (funded by NSF-IGERT and the UW)
Hands-on Training and Research in the NanoTech User Facility
Membership in Nanotech Student Association
Mentoring Program
Industrial Internship and Research at PNNL

***Graduation with* "Ph.D. in 'Home Department' and Nanotechnology"**