Cu(In,Ga)(S,Se)$_2$ Crystal Growth, Structure, and Properties

Angus Rockett

Department of Materials Science

The University of Illinois

1101 W. Springfield Avenue,

Urbana, IL 61801, USA

217-333-0417 arockett@uiuc.edu

With support from:

The National Renewable Energy Laboratory

University of Illinois

CIGS

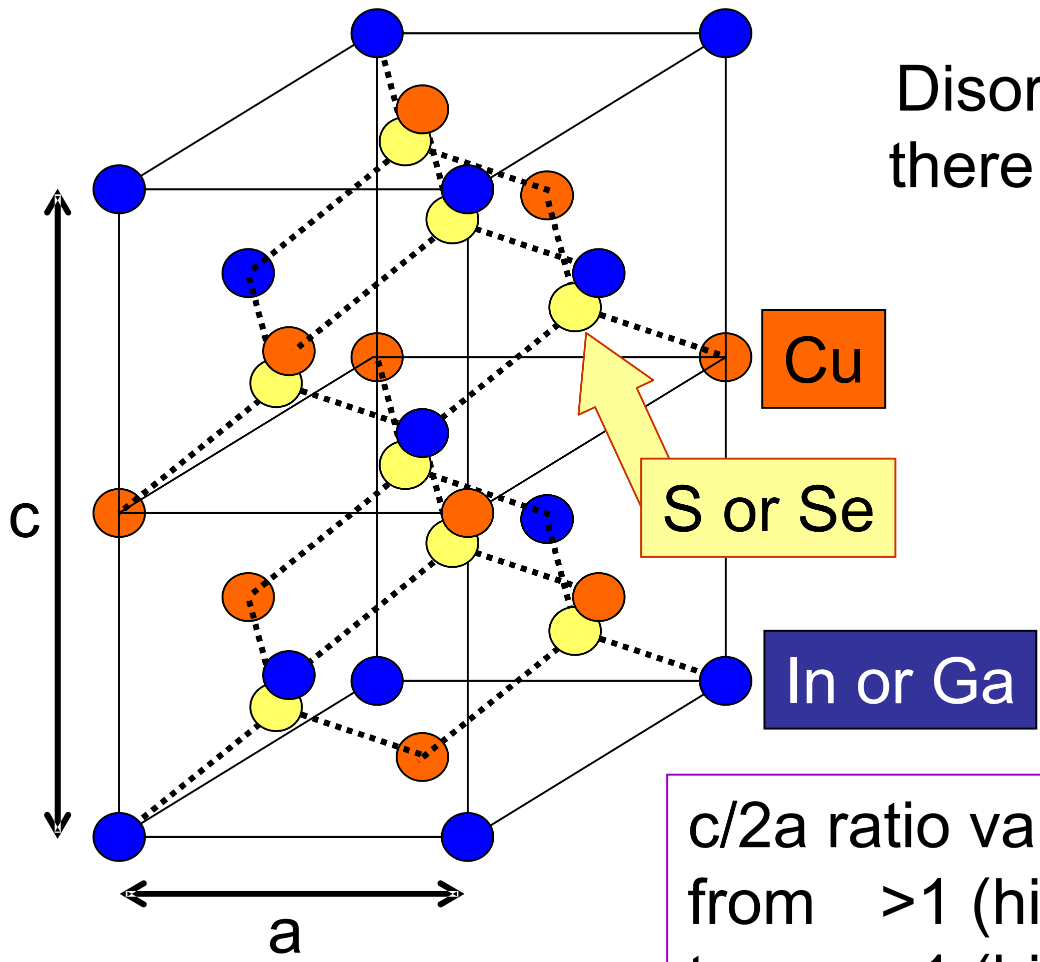
- Chalcopyrites have been proposed as spin-polarized electron emitters.
- They are also interesting for other applications including thin film transistors.
- Primary application -- solar cells

Useful Properties

- Engineerable energy gap in useful range (< 1eV to >2 eV).
- Very high optical absorption coefficient.
- Usable as polycrystals.
- Native defects “harmless” (all shallow).
- Few observable problems with impurities.

Basic crystallography and thermodynamics

Chalcopyrite $Cu(In,Ga)(S,Se)_2$



Disordering energy is low so there are many point defects

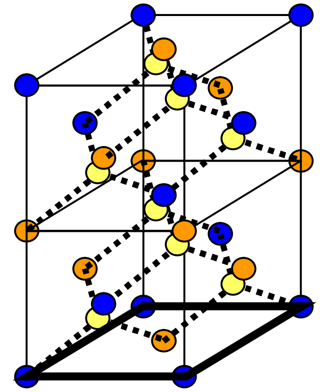
A polar compound so charged surfaces could be a problem

c/2a ratio varies
from >1 (high In)
to <1 (high Ga)

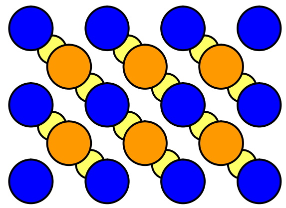
Chalcopyrite $Cu(In,Ga)(S,Se)_2$

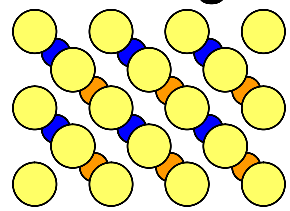
Metal

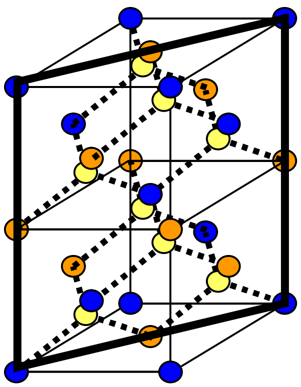
Chalcogen

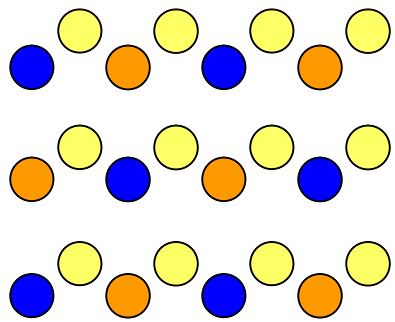


Polar

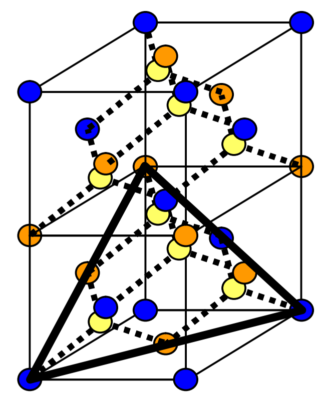




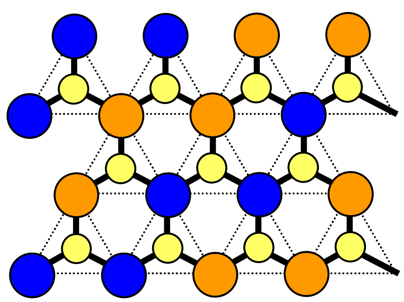


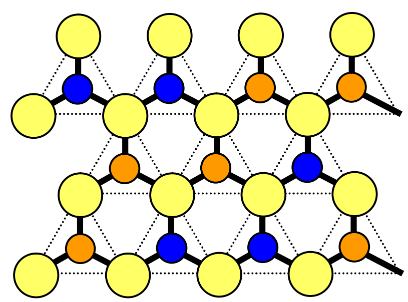


Non-polar



Polar





Metal

Chalcogen

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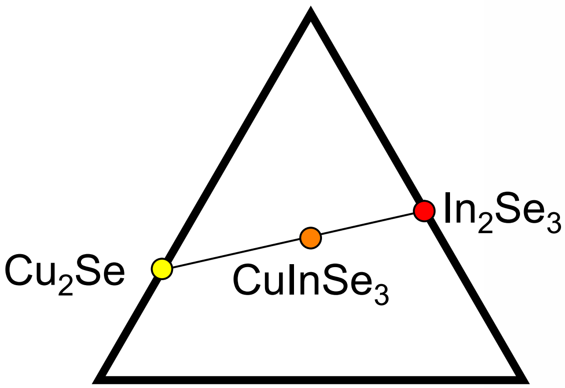
Ternary Phase Diagram

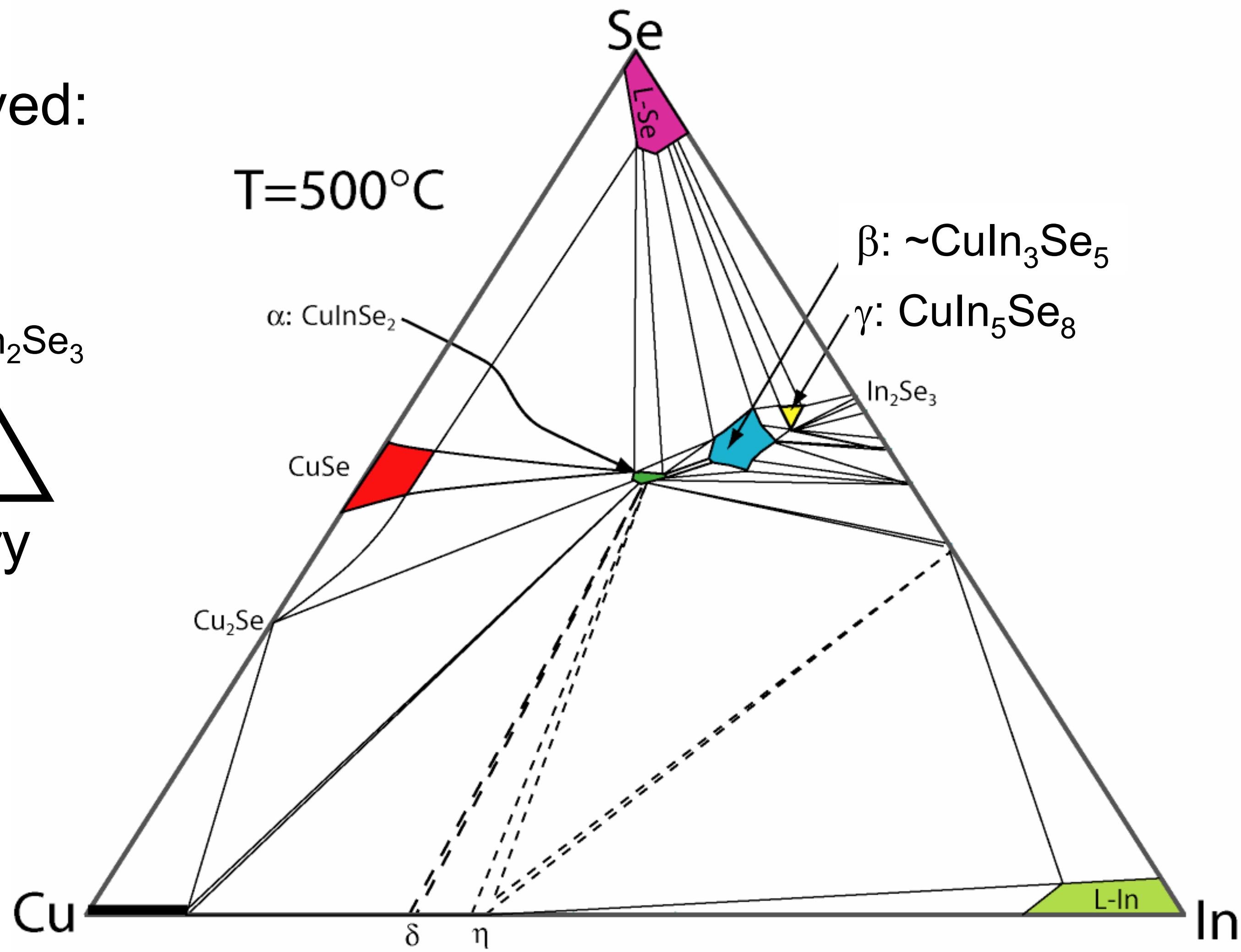
…and right away we know we are in trouble.

What is observed:



Pseudobinary

…is valence compensating



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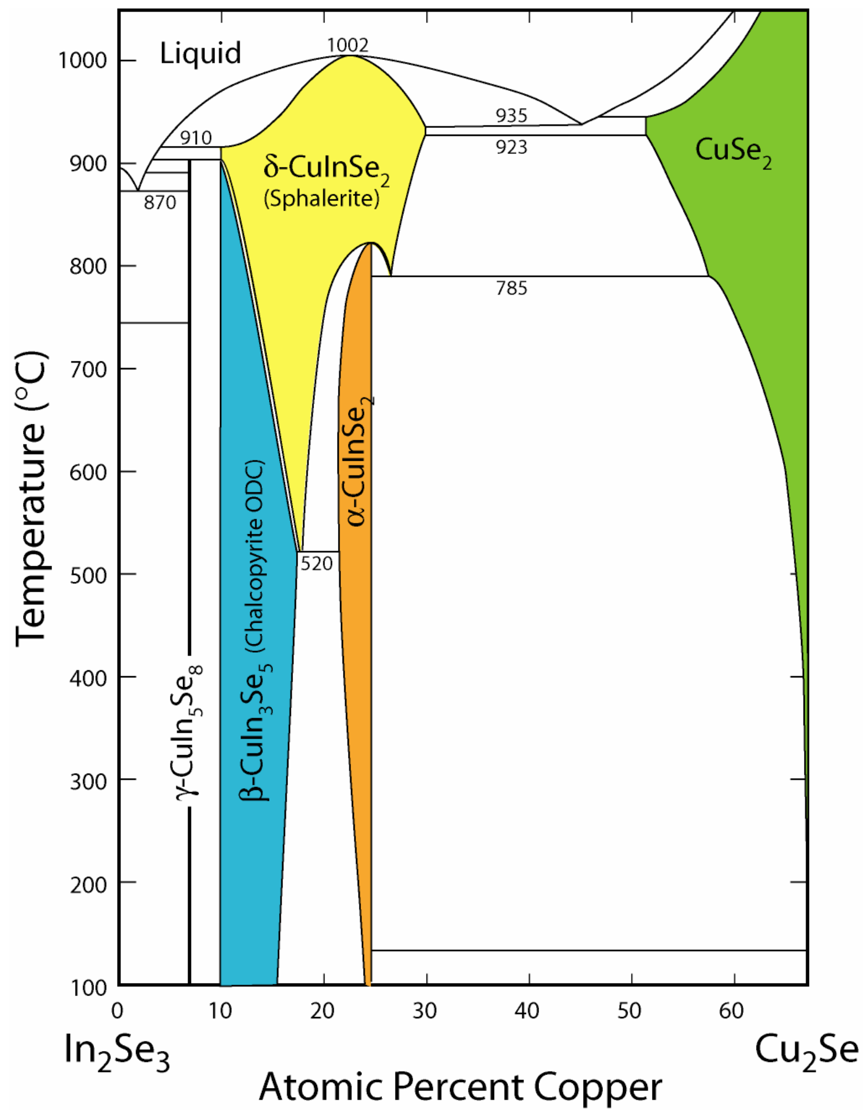
Pseudobinary Phase Diagram

Note: extended solubility in α phase.

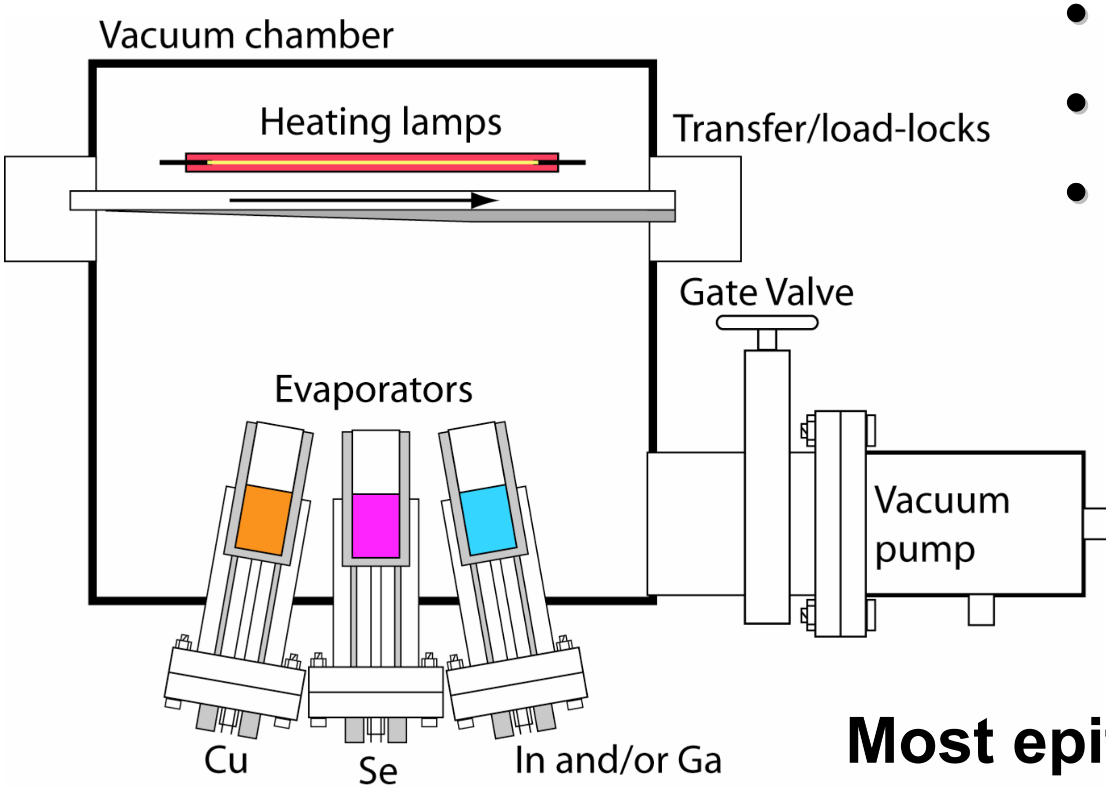
Low-temperature chalcopyrite-sphalerite transition suggests low cation ordering energy.



Deposition Methods

Evaporation

- Multisource Evaporation

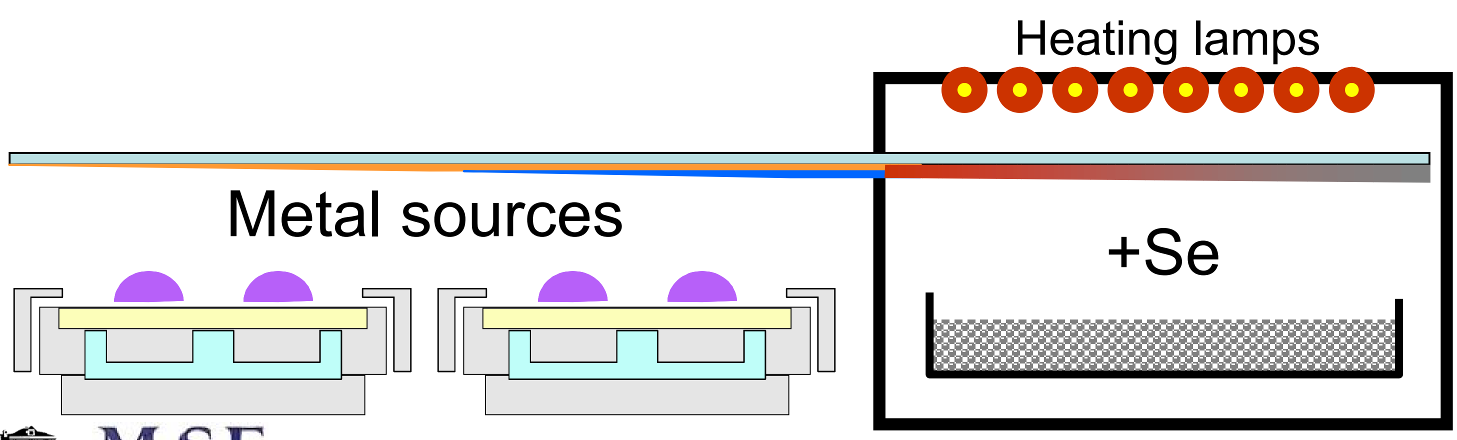


- High rate
- Easy control
- Difficult to scale
- High temperature process

Most epitaxy by MBE
Most solar cells this way

Selenization

- Deposit metals separately
- React with a Se source (Se vapor or H_2Se).
- Similar processes with sulfides
- Sequential, easy to control
- High film stress
- Reaction of metal layers & phases formed are critical, processes complex.

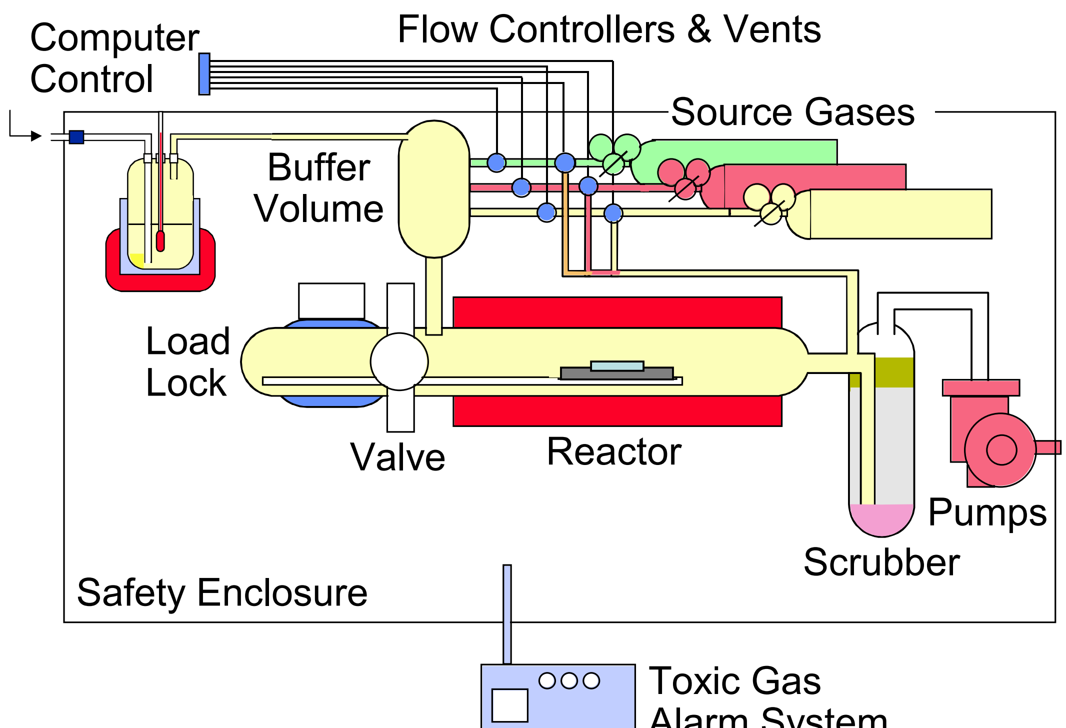


MOCVD

Hydrogen selenide
Trimethyl Ga or trimethyl In
Complex Cu compound: use bubbler source. Low rate.

Epitaxy by MOCVD
at Hahn Meitner Institute

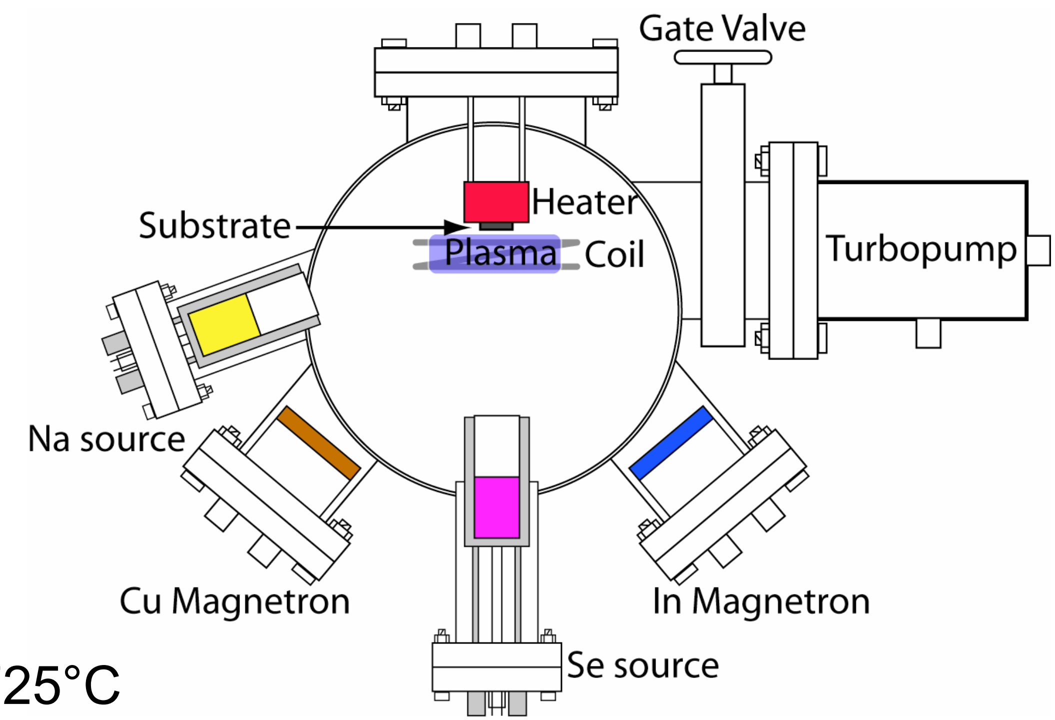
Best growth:
Cu-rich films
500-550°C



Hybrid Method

Growth Process:

- Similar to MBE
- Evaporate Se
- Sputter metals
- Optional rf coil for ionization



Growth rate ~ 1μm/hr.
Substrate temperature: 550-725°C

Cu-Ga target for Cu(In,Ga)Se_2

Cu target for pure $CuInSe_2$

Cu and Ga targets for $CuGaSe_2$

Epitaxy on GaAs:

Typical hole mobility
~280 cm^2/V-sec

Typ. Carrier Lifetime:
~ 0.4 nsec

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Band Structure

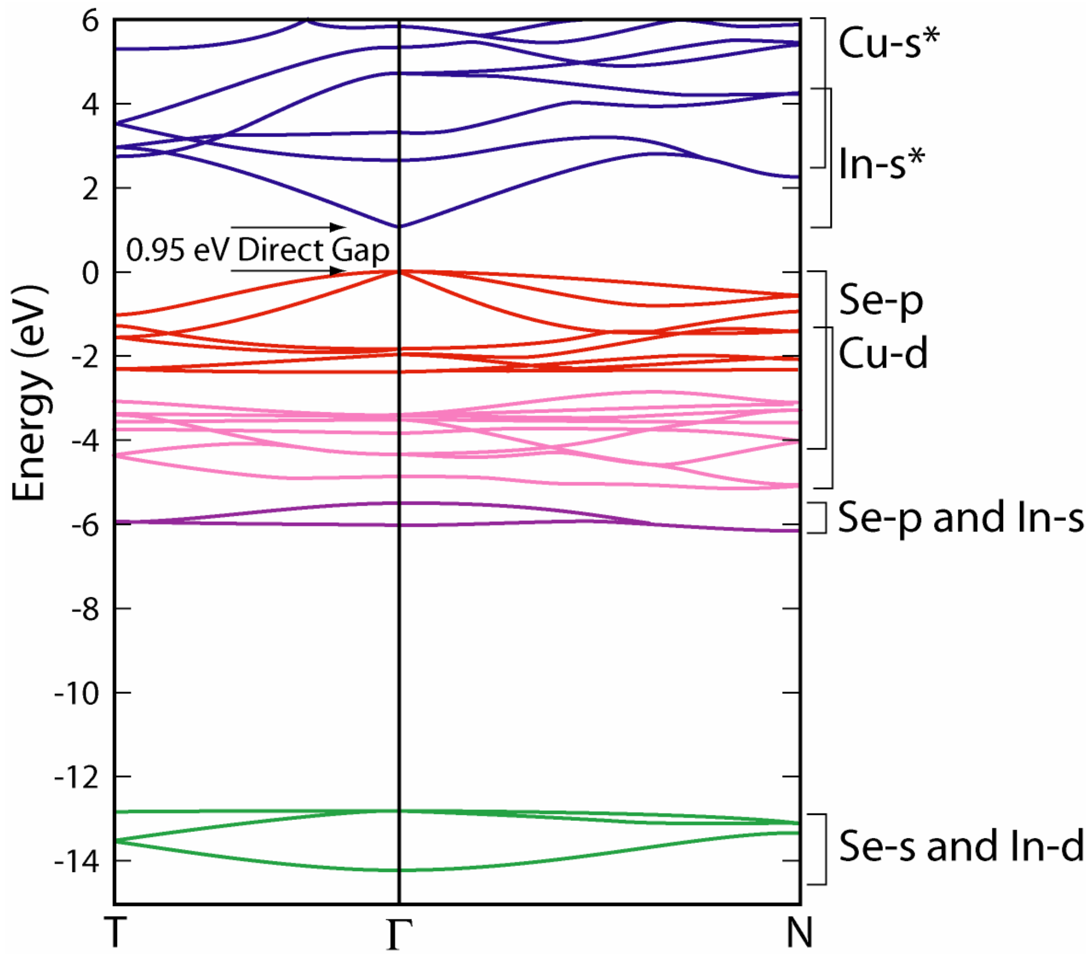
Band Structure - Theory

Se-S alloys mostly affect valence band edge.

In-Ga alloys mostly affect conduction band.

Cu-Ag alloys have minor effects on both bands.

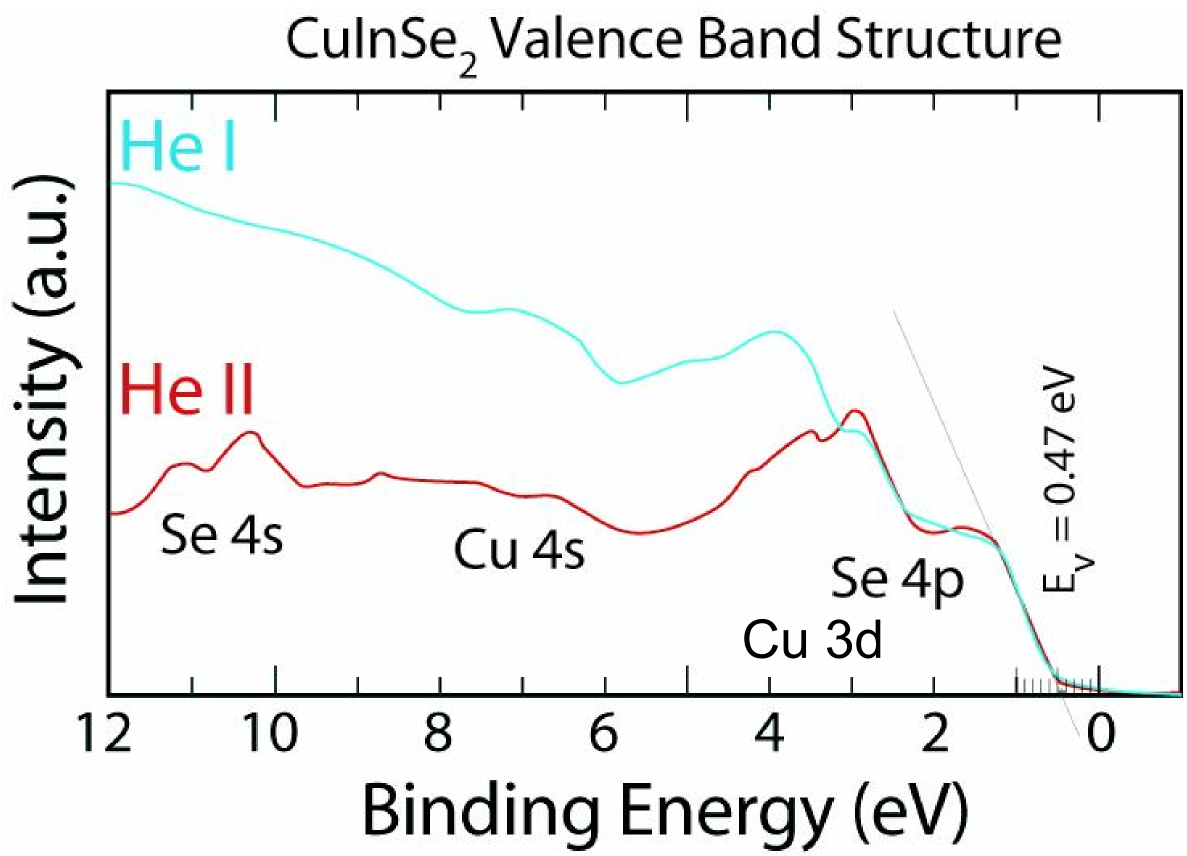
Gaps are low because of Se-p : Cu-d repulsion.



After S.B. Zhang, S-H. Wei, A. Zunger, and Y. Katayama-Yoshida, Phys. Rev. B 57(16), 9642 (1998).

Experimental UPS

- Se capped surface $(112)_{Se}$ cleaned thermally shows $E_f - E_V \sim 0.47$ eV.
- Agrees well with data from other labs



Optoelectronic Properties

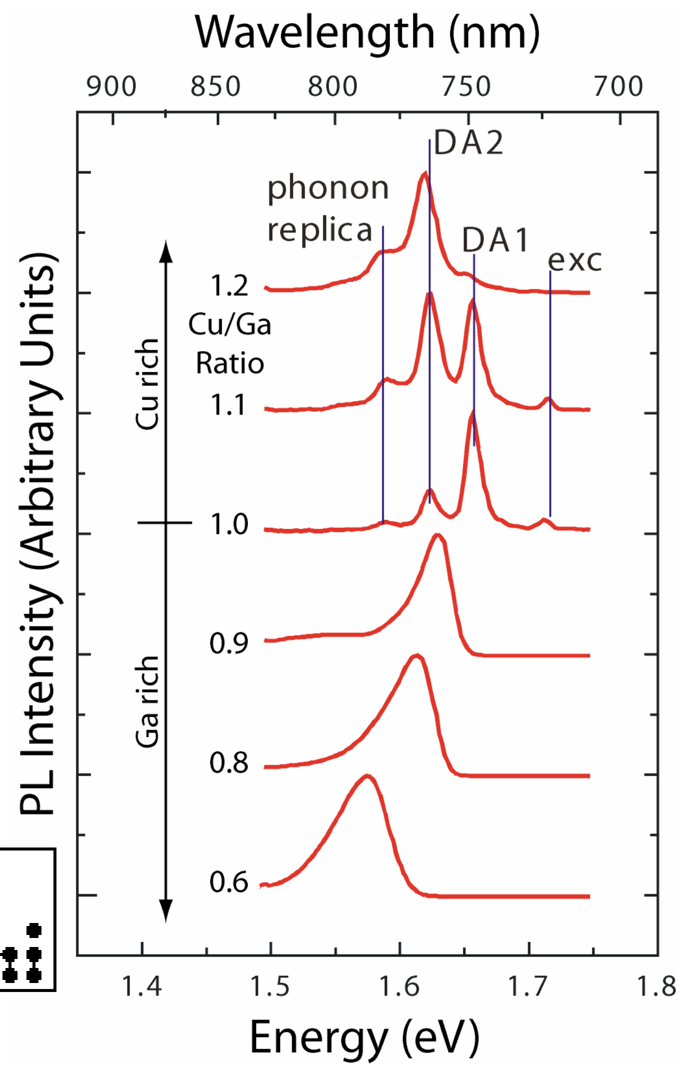
Photoluminescence Data

Cu-rich films show sharp emissions:

- Donor-acceptor emissions
- Weak band-band emission

Group-III rich films show broad emissions.

Polycrystals same as epilayers



Data: S. Siebentritt et.al.
Hahn Meitner Institute

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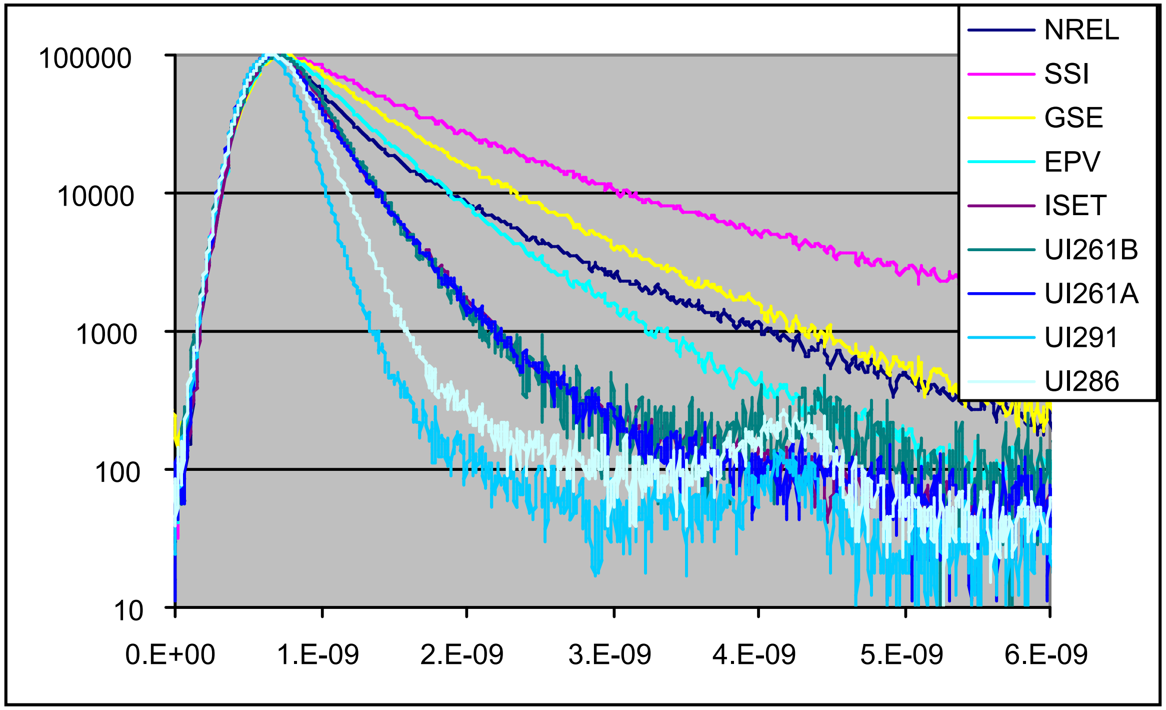
Photoluminescence Lifetime

Lifetimes 0.2-4 nsec

Consistent with direct-gap band structure

Microsecond decay (not shown shows deep state)



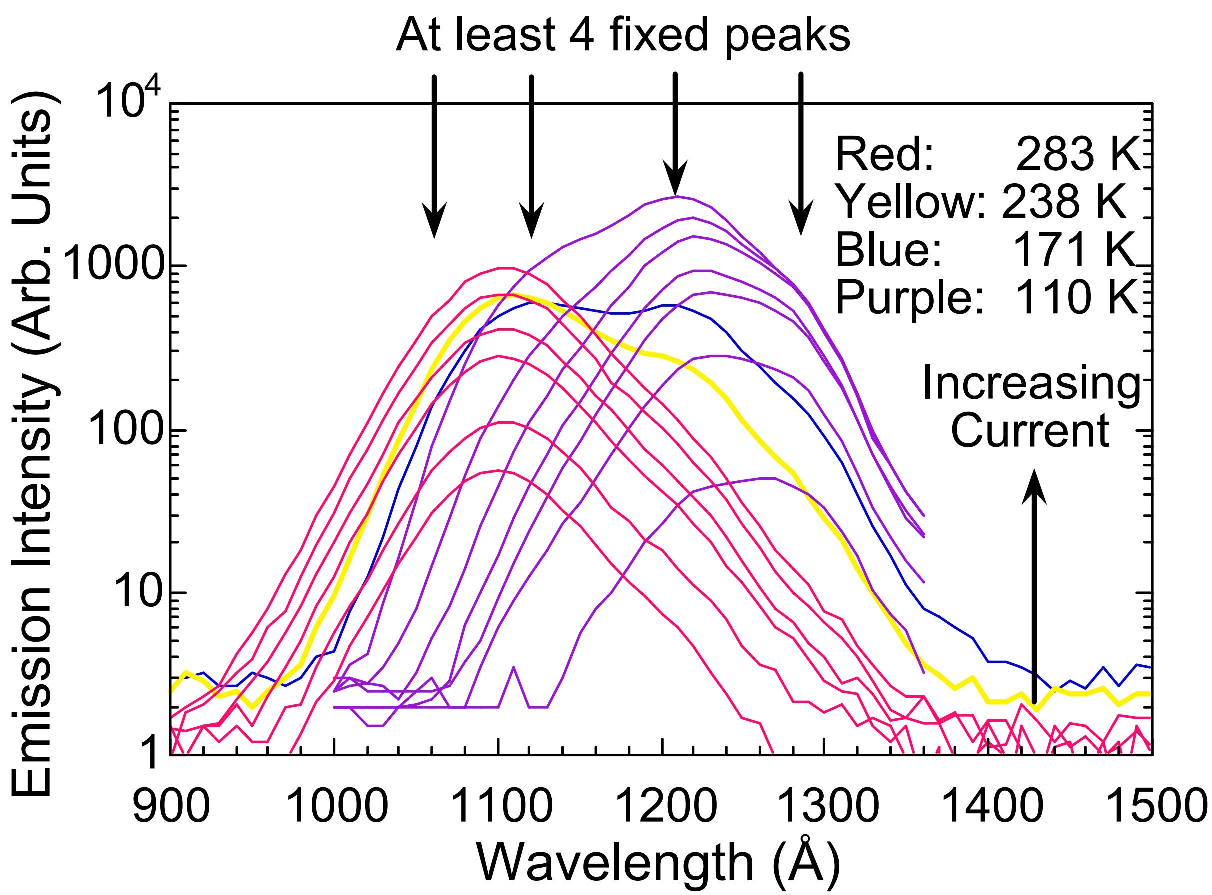
Epilayers have short lifetimes. Suggests minority carrier traps.

Electroluminescence

Defect-to-defect, not band-to-band recombination.

Photon energy does not track the gap change with Ga.

Similar to CIS PL data.

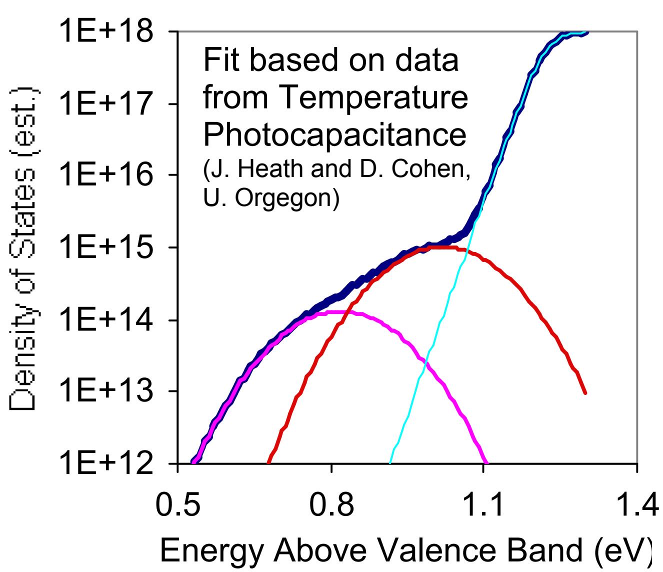


Experimental Data for deep levels

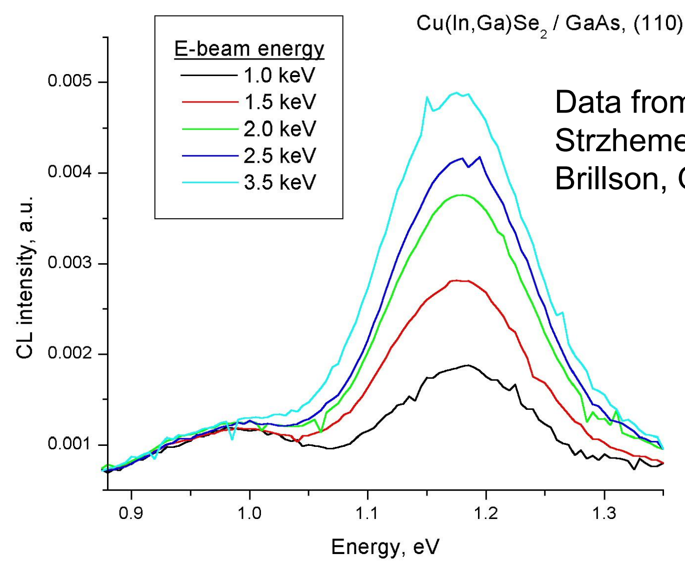
Thermophotocapacitance

Cathodoluminescence

	IEC Device		UIUC Epilayer Device		Both Layers	
	Defect 1	Defect 2	Defect 1	Defect 2		
Energy above VBE	0.8	0.9	0.8	1	E(gap)	1.22
Width	0.13	0.15	0.13	0.15	Band Tail width	0.022
Concentration	1.00E+14	3.50E+14	1.00E+14	1.10E+15	Band Tail DOS	1.00E+18



Quantitative estimate of defect state densities.

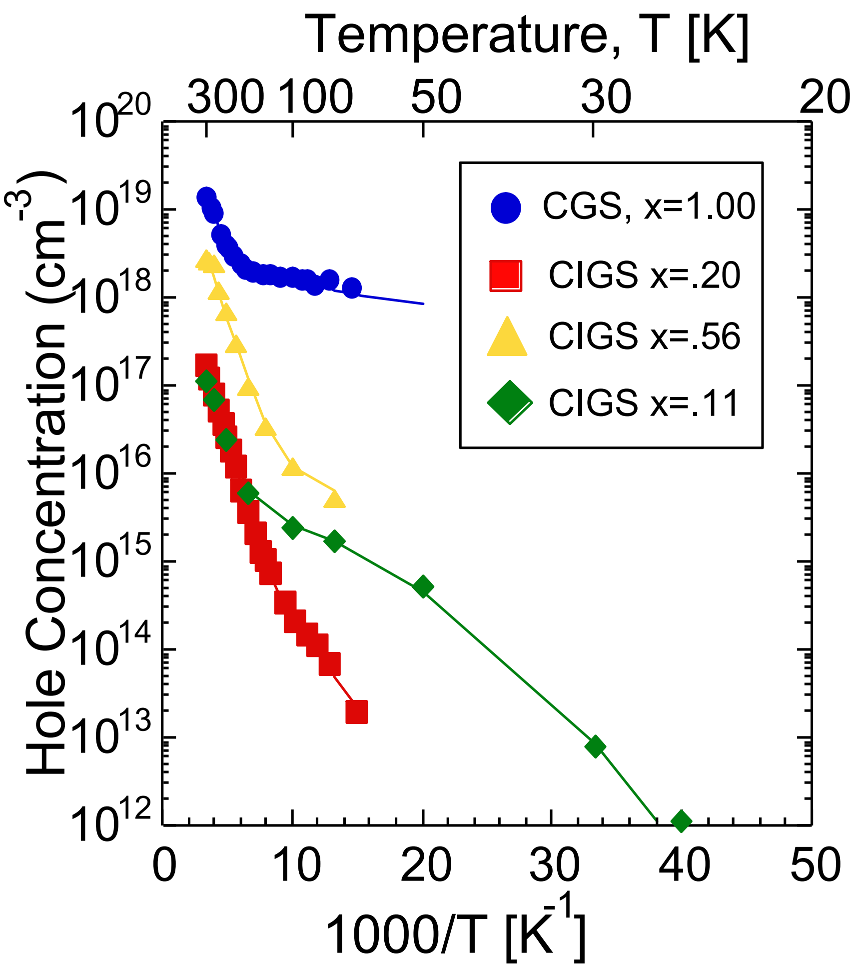


Data from Y. Strzhemechny and L. Brillson, Ohio State U.

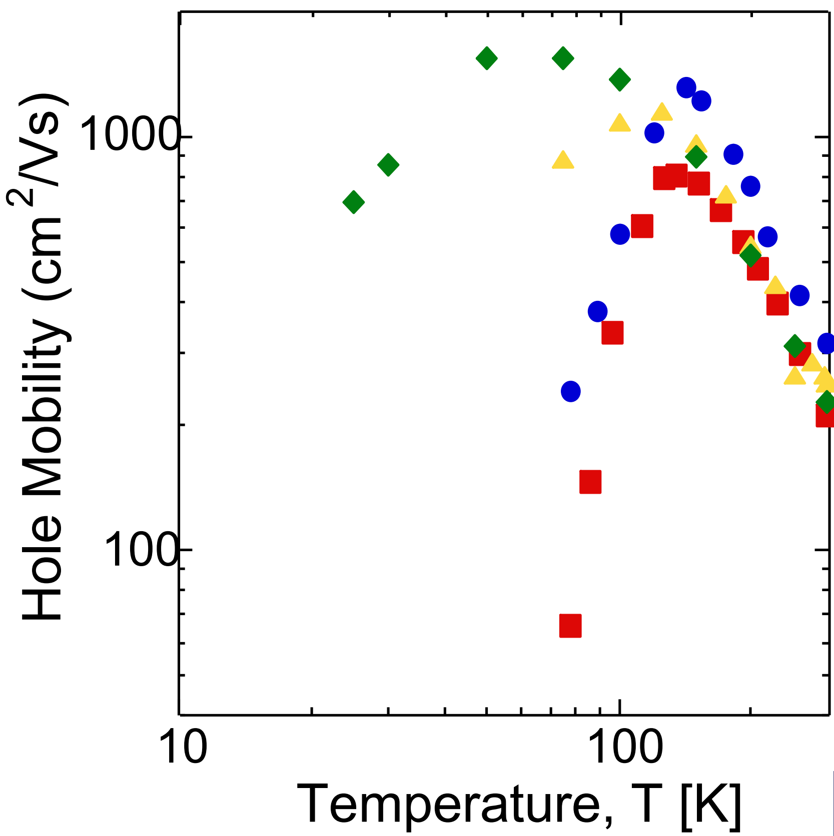
Subgap states produce clear CL emission spectra

Hall Effect

Carrier Concentration:

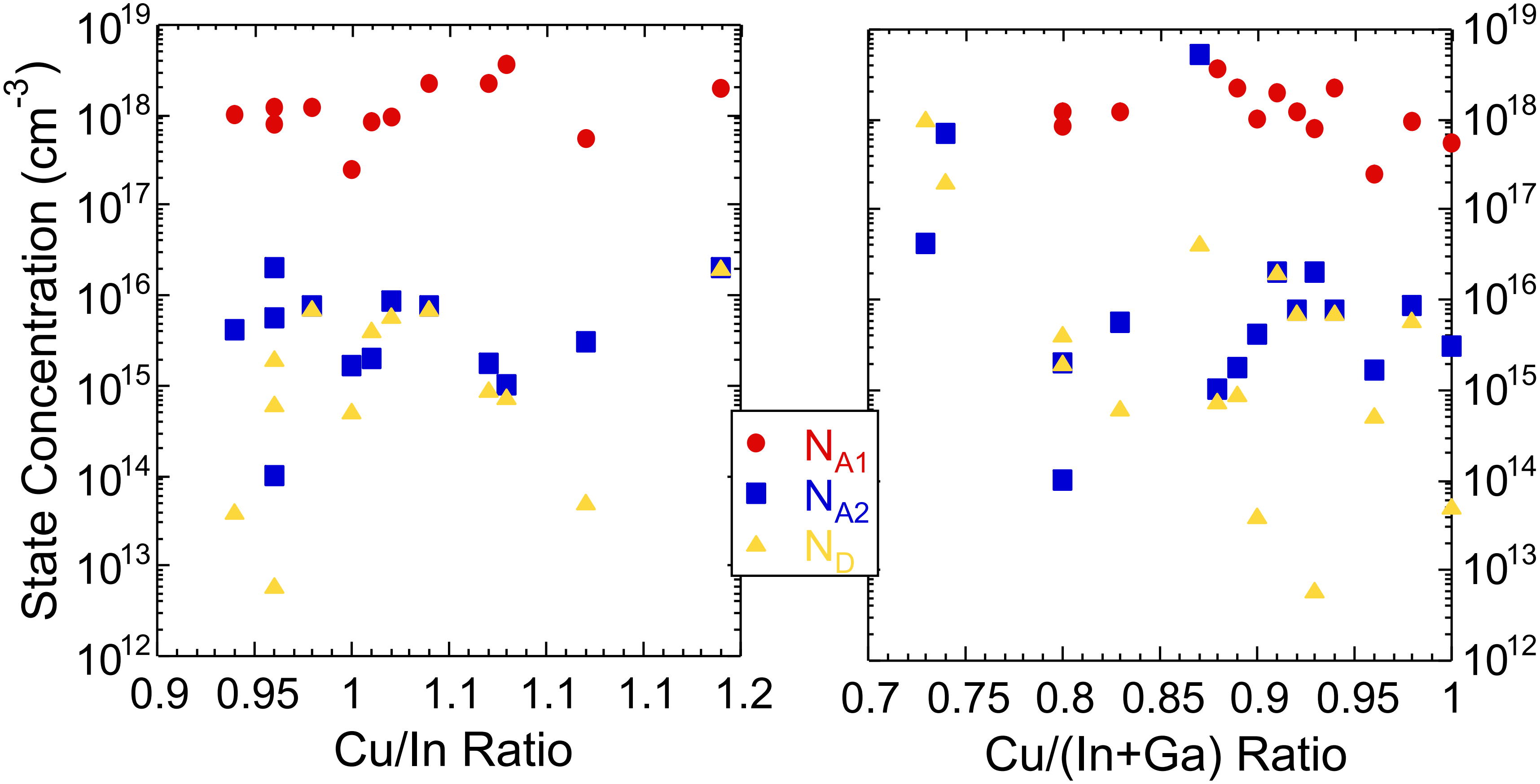


Hole Mobility:



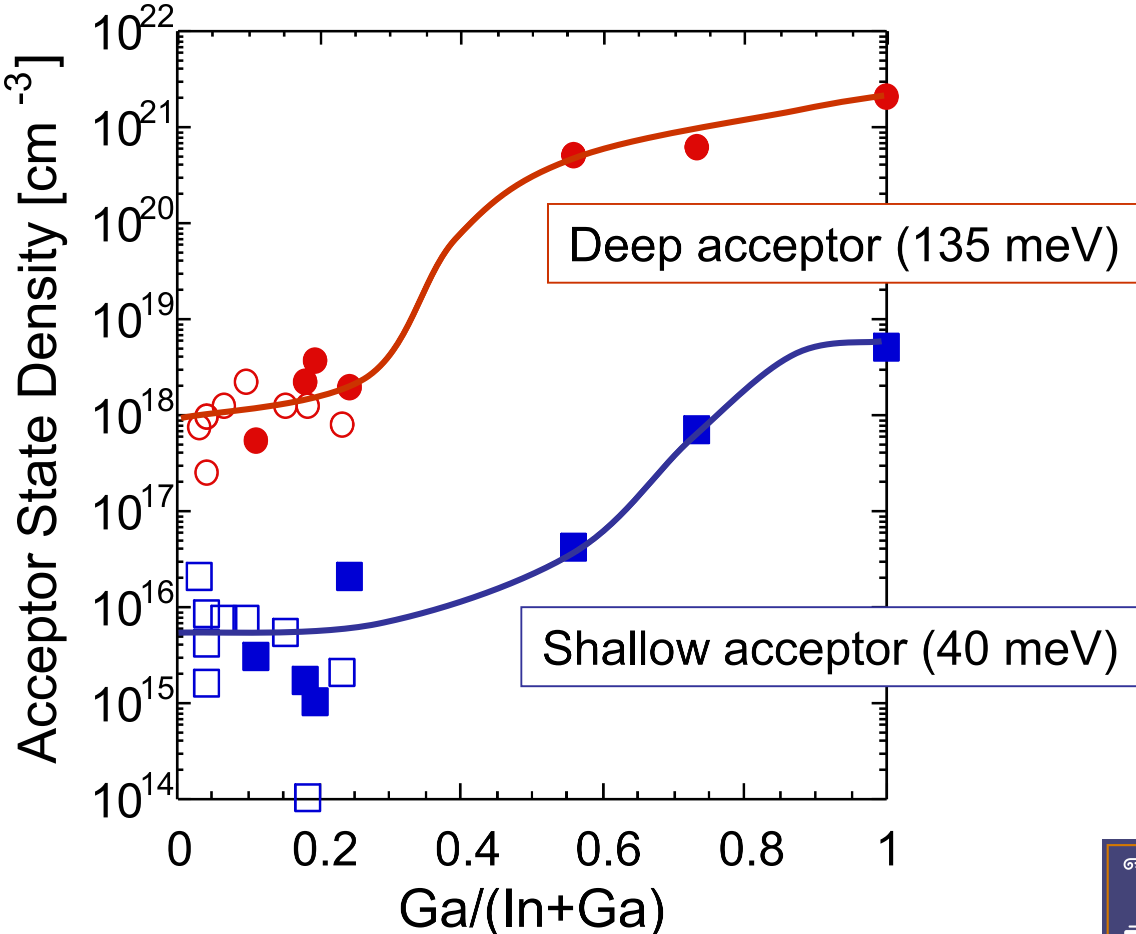
Hall Effect -- vs. composition

No change in electrically-active defects with Cu/III composition.



Hall-effect -- vs. composition

…except for Ga, which increases p at high Ga contents.



Open points: Ga gradient
Closed points: uniform Ga

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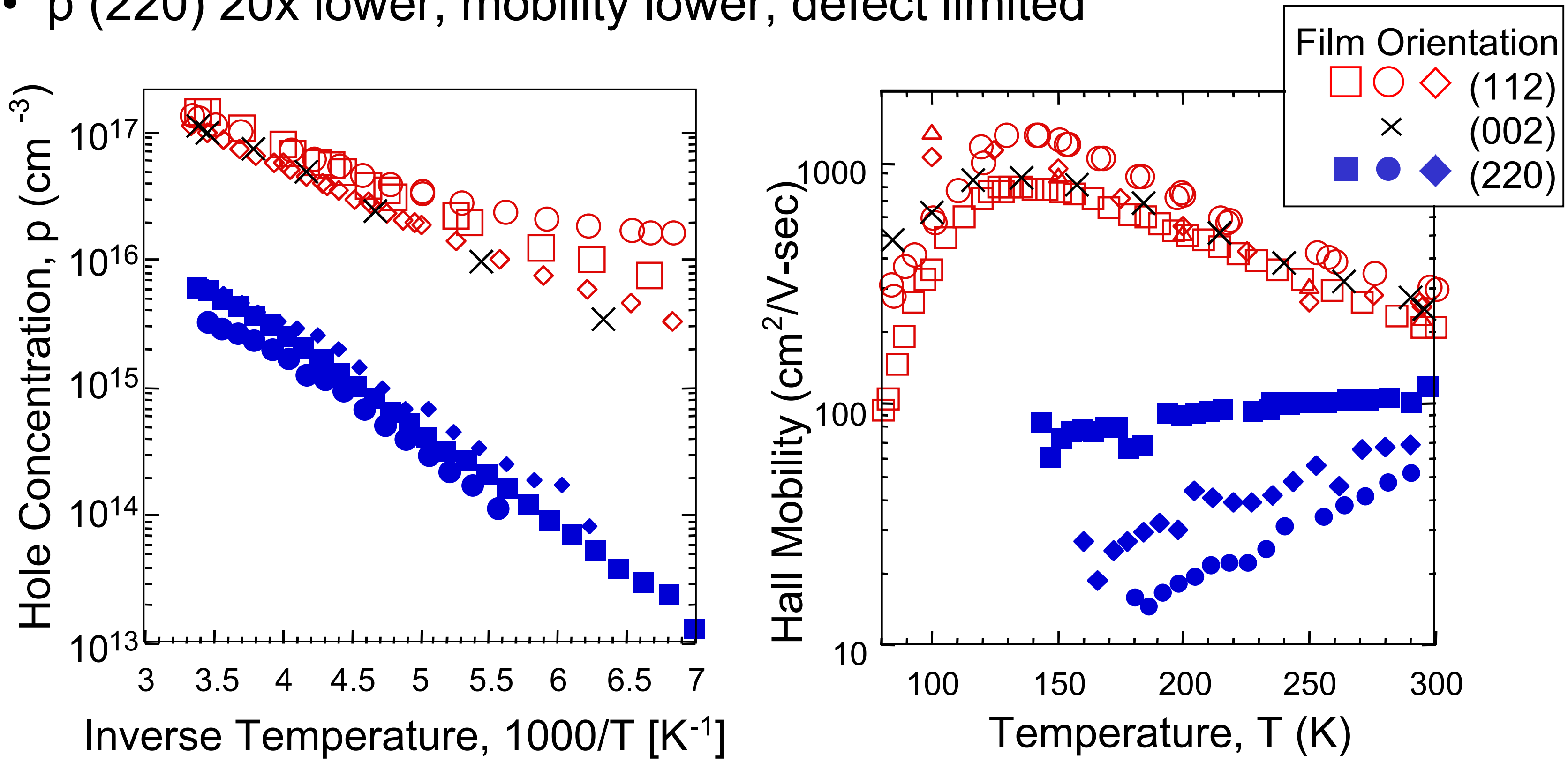
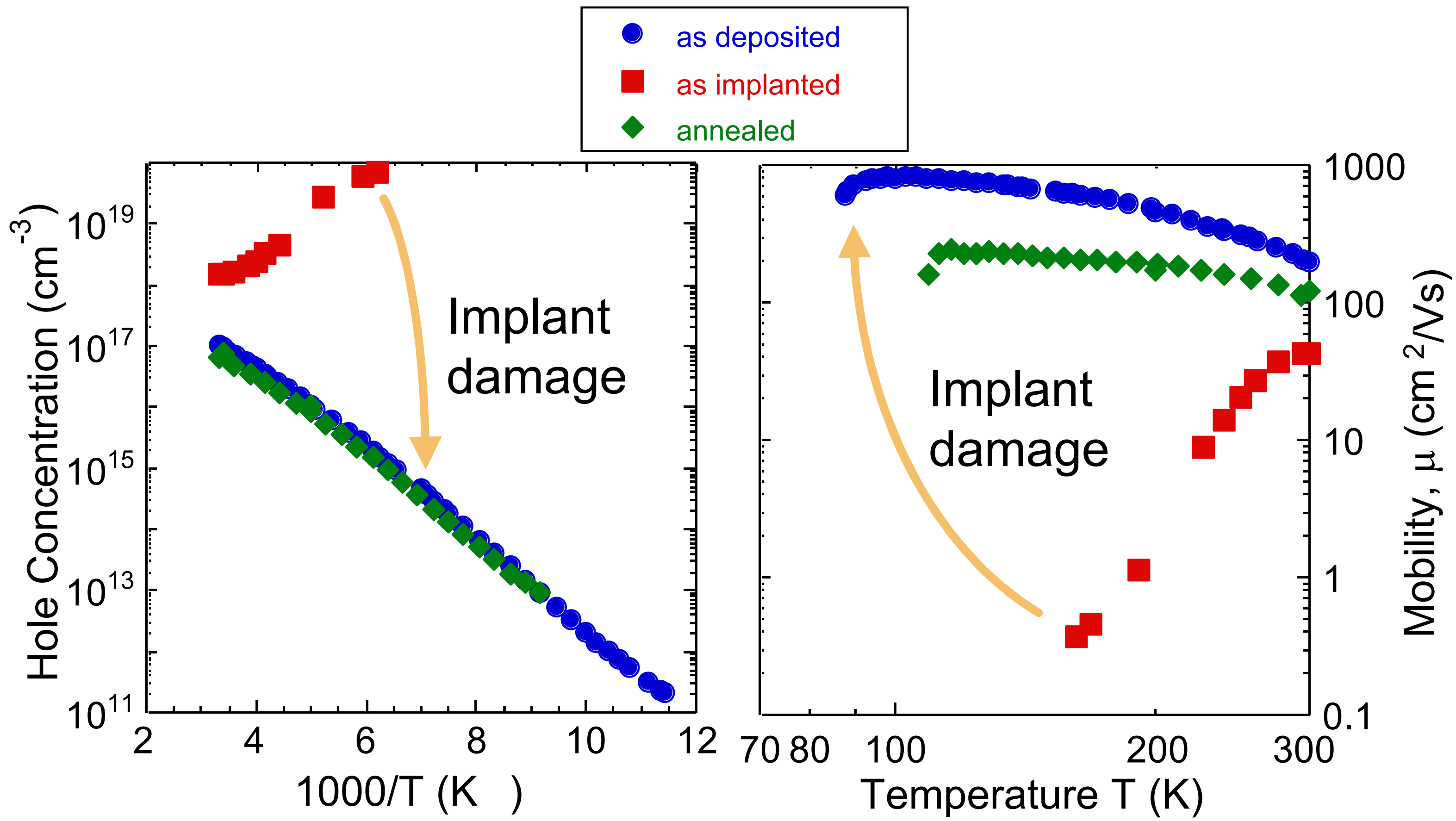
Growth Orientation Effects

- (112) and (002) very similar, phonon scattering for (112) and (002)
- p (220) 20x lower, mobility lower, defect limited



Implant Changes

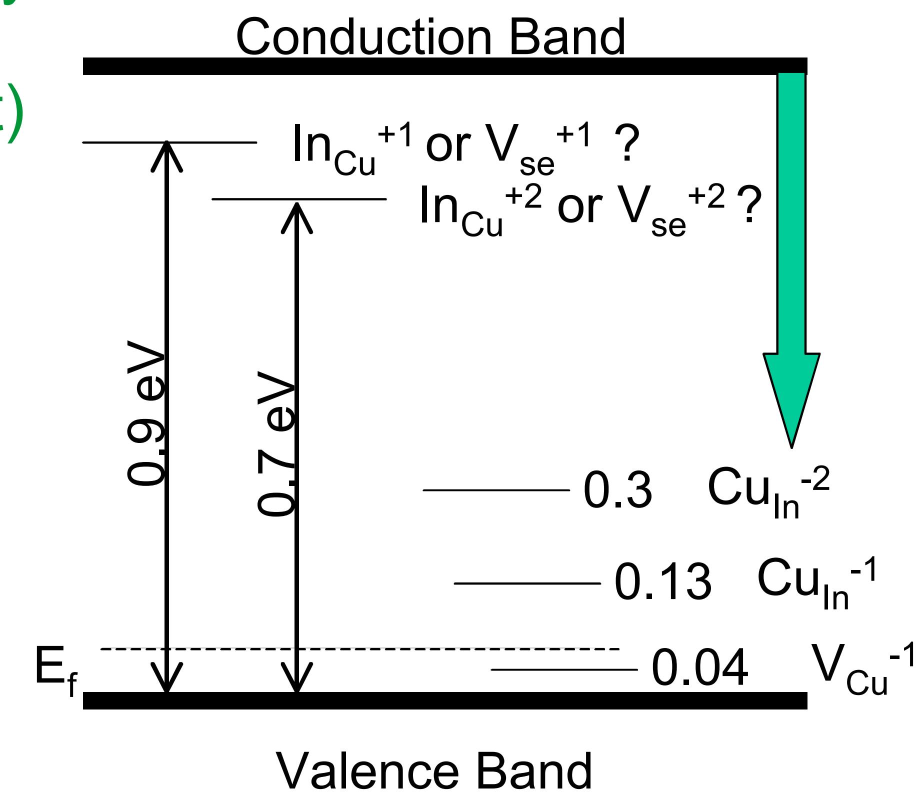
Low dose Se implant -- mostly reversible changes.



Cr implant similar

Point Defects Summary

- Shallow acceptor: Cu vacancy
- Deep acceptor: Cu_{In} (divalent)
- Defects 0.8 and 1.0 eV above valence band: probably Se vacancy
- Above do not shift with Ga/(In+Ga)
- Additional deep states?



Surface Energy & Growth Mechanisms

Surface Morphology

Summary:

Best epitaxy on GaAs (111).
Rough surfaces on GaAs (110).

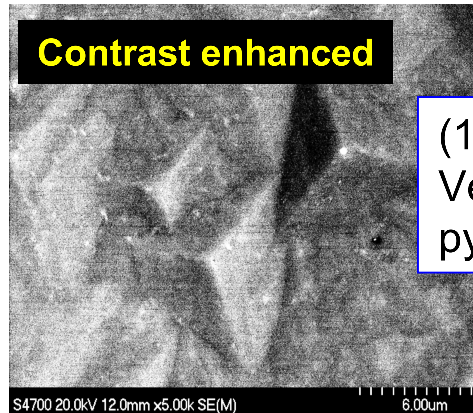
Epitaxial temperatures:

T_s = 540 ° C (220); 640 ° C (100); and 700 ° C (112)

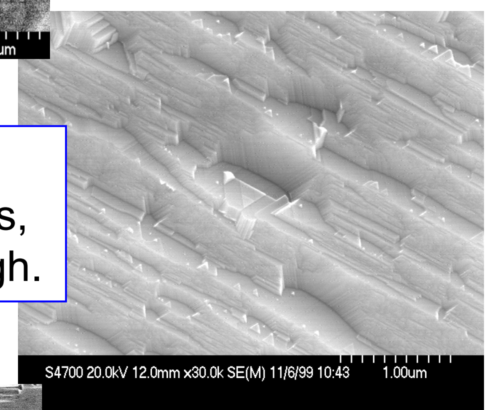
Pure $CuInSe_2$:

Ga diffuses from the substrate

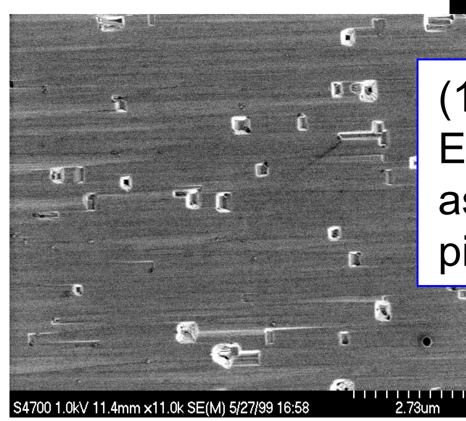
Kirkendall voids form at the interface in the GaAs substrate.



(112) close-packed
Very low angle (<1°) pyramidal facets.



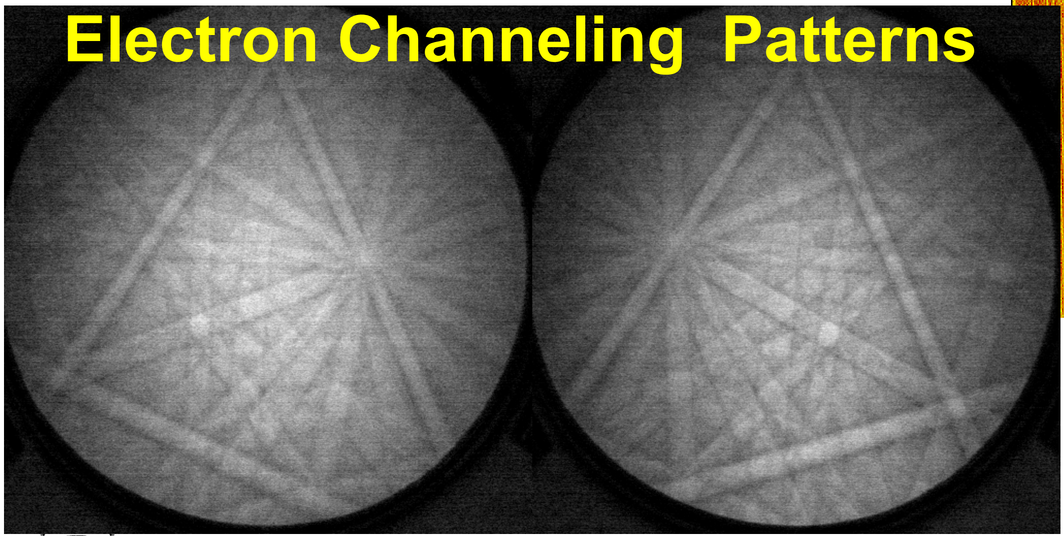
(220)/(204) surface
Facets to (112) planes, one smooth, one rough.



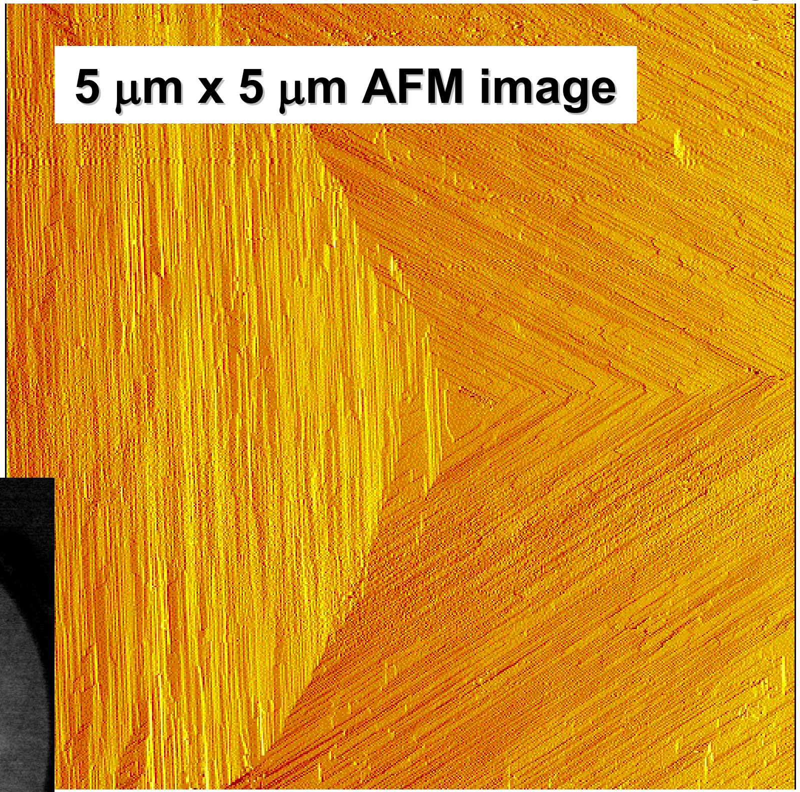
(100)/(002) surface
Elongated ripples with asymmetric rectangular pits sometimes present.

$(112)_{Se}$ Close Packed Surface

- Growth by step nucleation and propagation
- Very flat
- 180° growth twins ~40 μm apart



Steps: 1-3 ML high

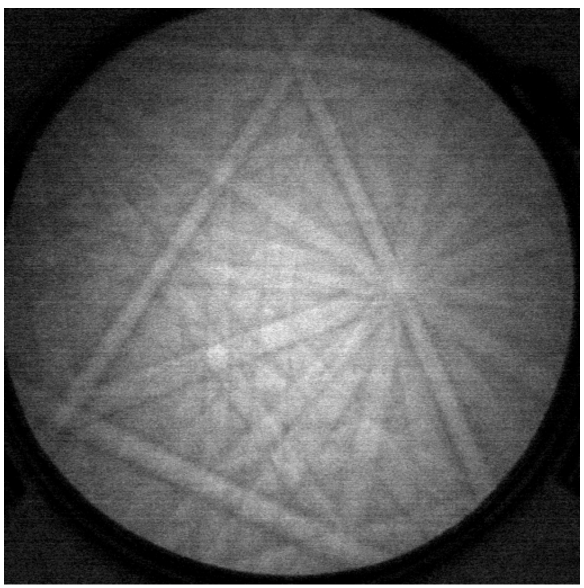


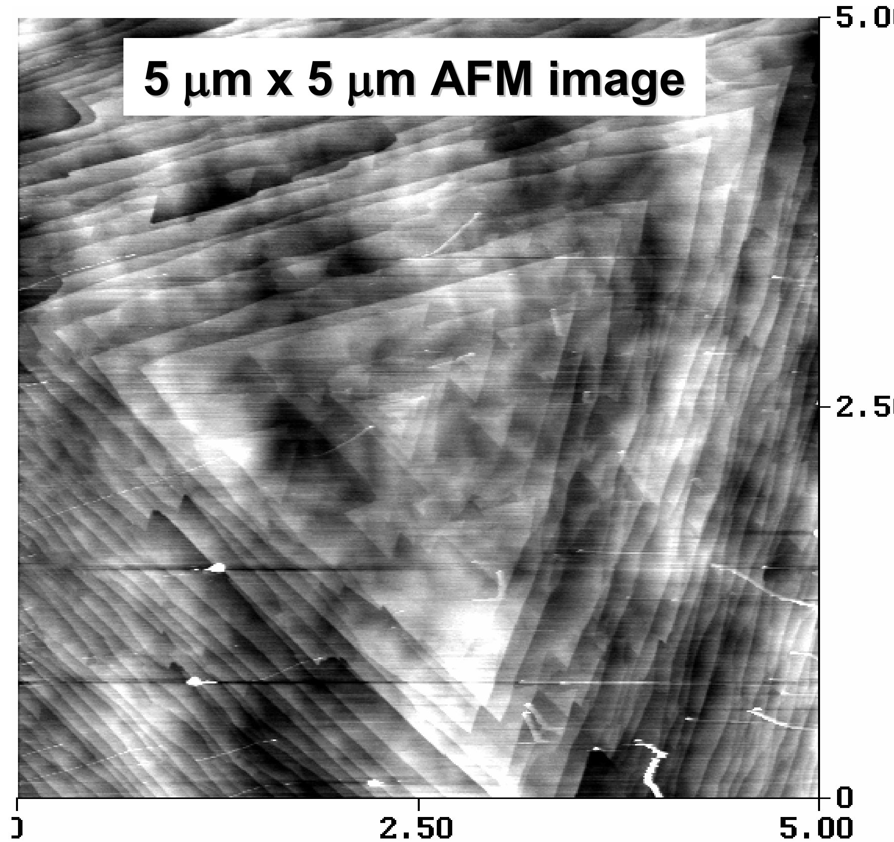
Very triangular facets, strong step orientation

(112)$_{Metal}$ Close Packed Surface

Steps: 1-2 ML high

- Growth by step nucleation and propagation
- Very flat
- No growth twins over the entire surface!

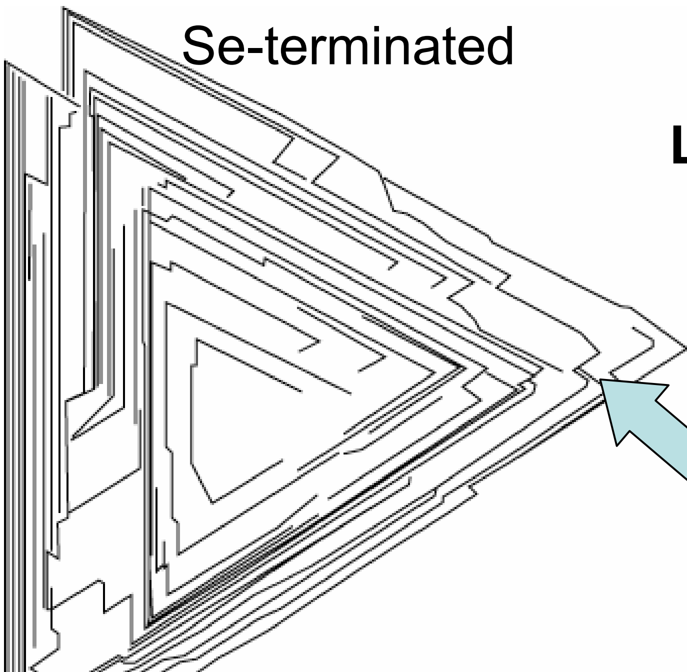




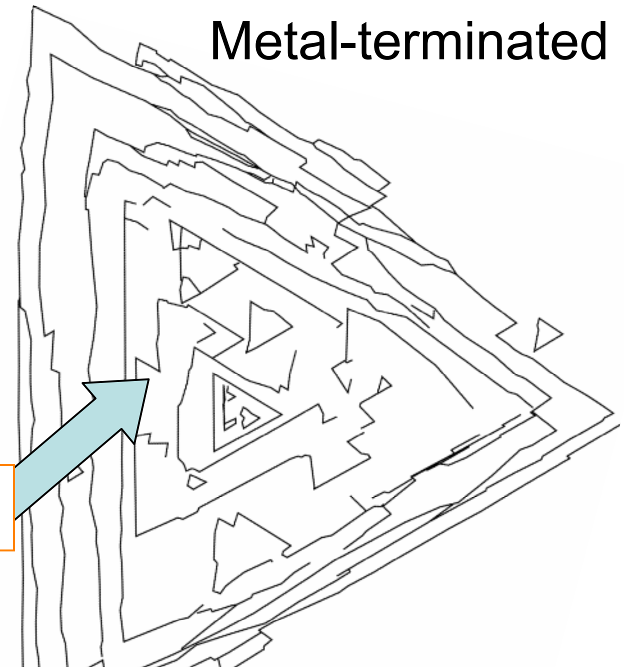
Very triangular facets, strong step orientation

(112) Surface Steps Compared

- Both surfaces show triangular pyramids -- very similar



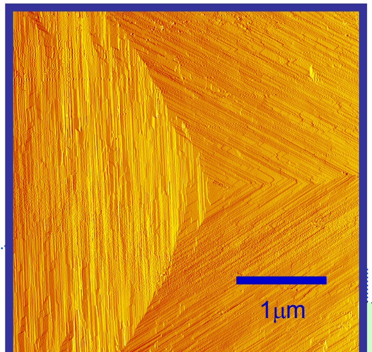
Layers nucleate near terrace edges!



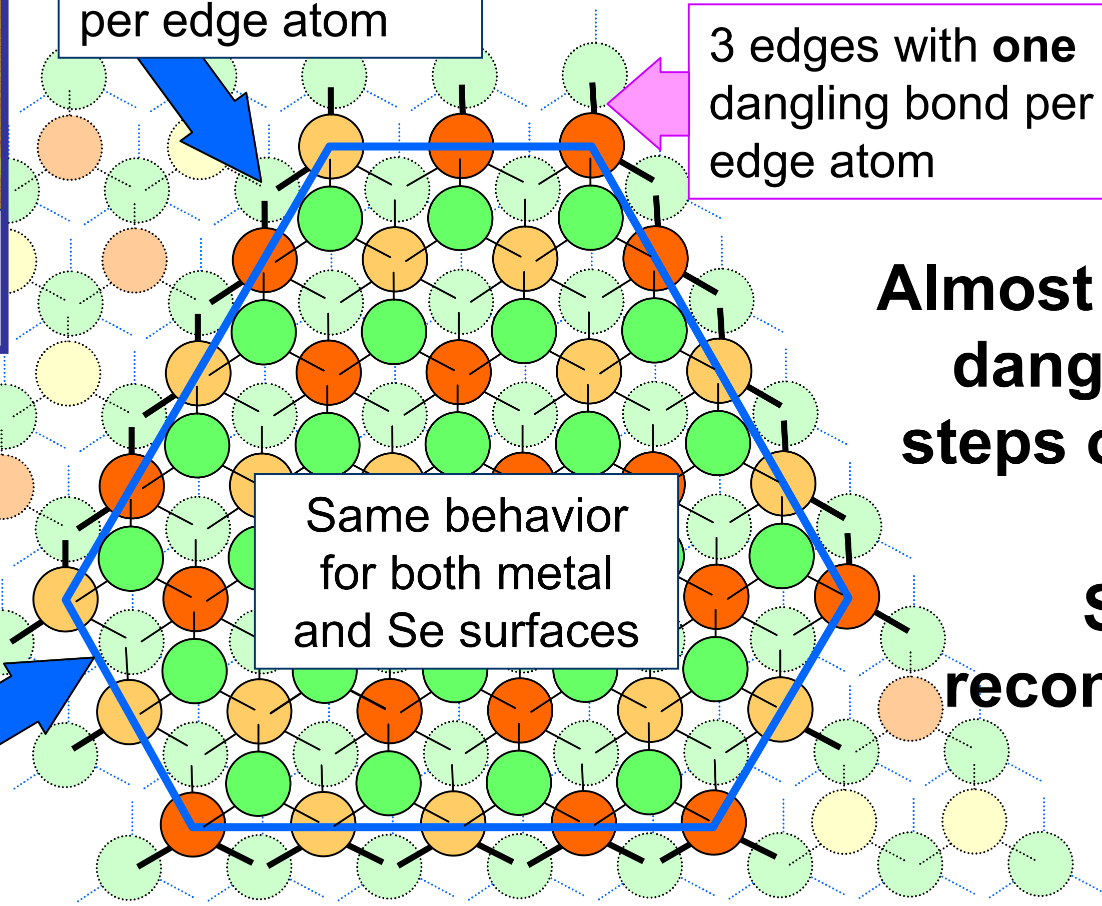
Inside corners!

One type of step dominates
More preference on Se-terminated surface

Implications for Steps



One step type dominates

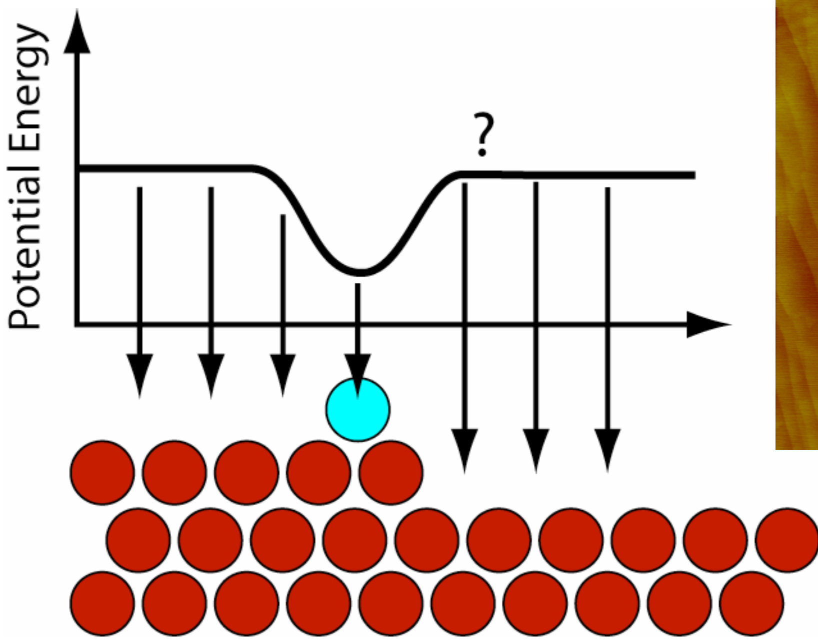


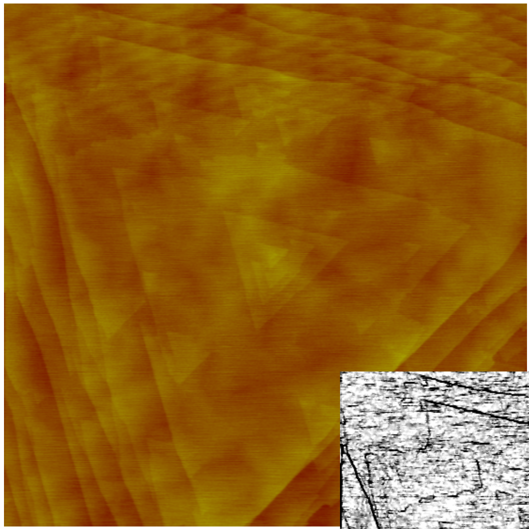
Almost no single dangling bond steps observed!

Step-edge reconstruction implied

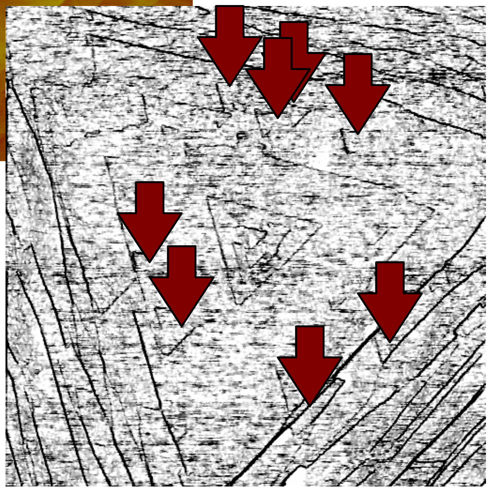
Layer Nucleation

Nucleation at step edges implies a barrier to atoms crossing downward over steps or binding to the upper step edge.





Nuclei

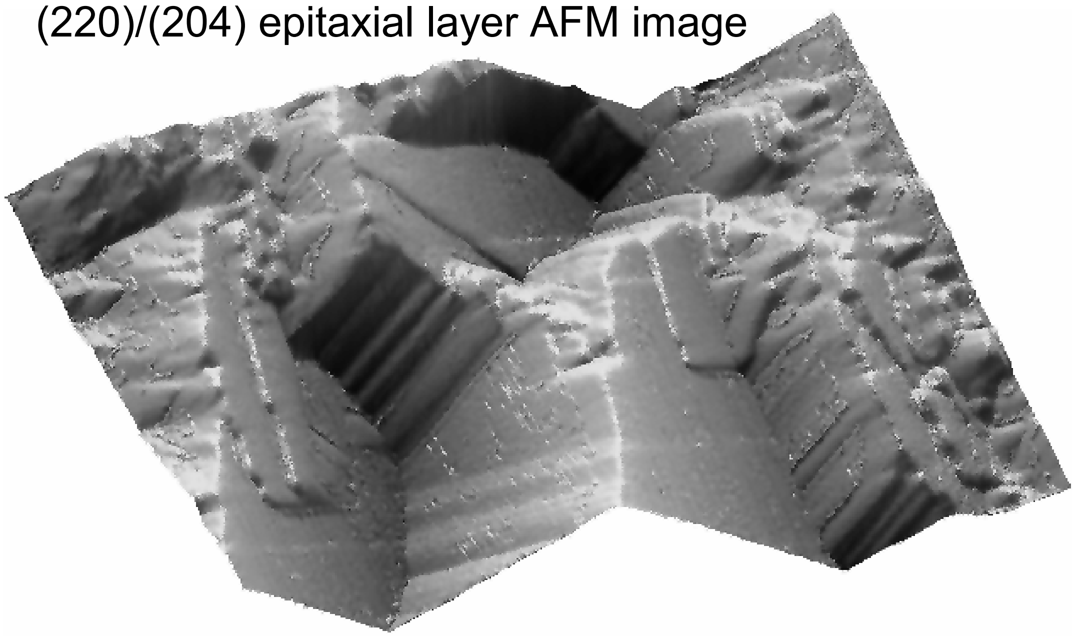


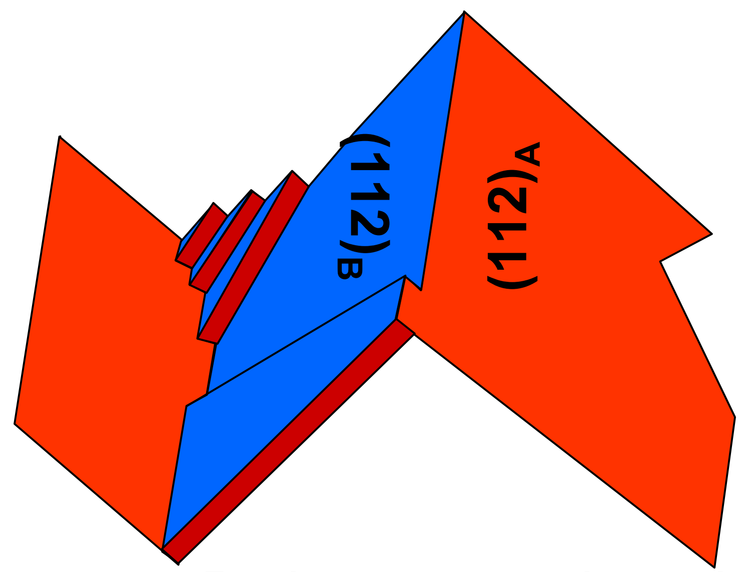
(220)/(204) Oriented CIGS

Layers facet spontaneously into **polar** (112) type planes.
Smooth facets alternate with rough facets.

Indexing surface planes shows smooth planes are metal terminated

(220)/(204) epitaxial layer AFM image





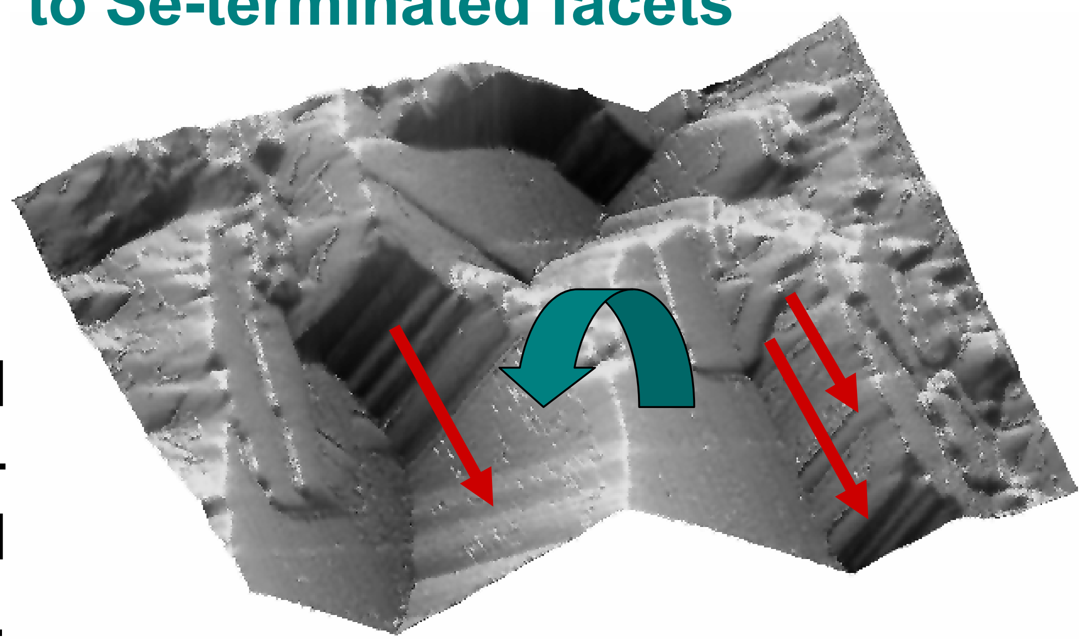
Red: metal terminated
Blue: Se terminated

(220)/(204) Oriented CIGS

- Implication of the smooth/rough surfaces:

Diffusion transfers atoms to Se-terminated facets

Nucleation and growth on Se-terminated surface.

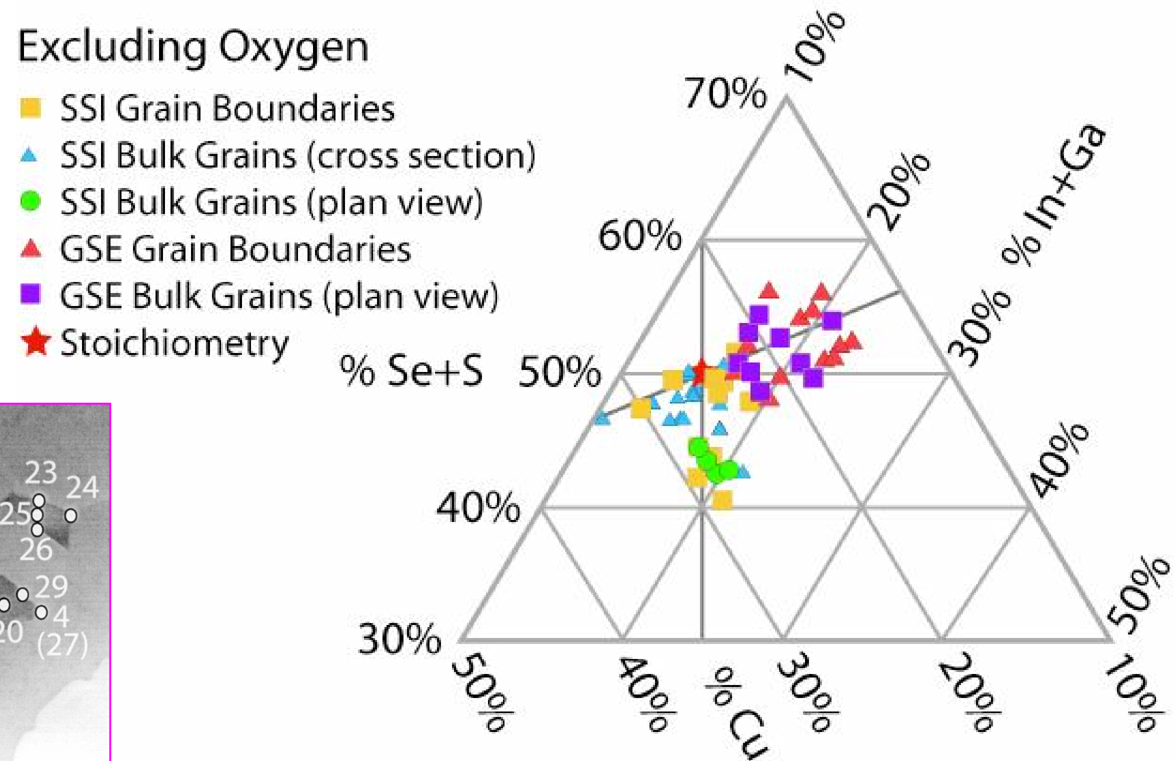


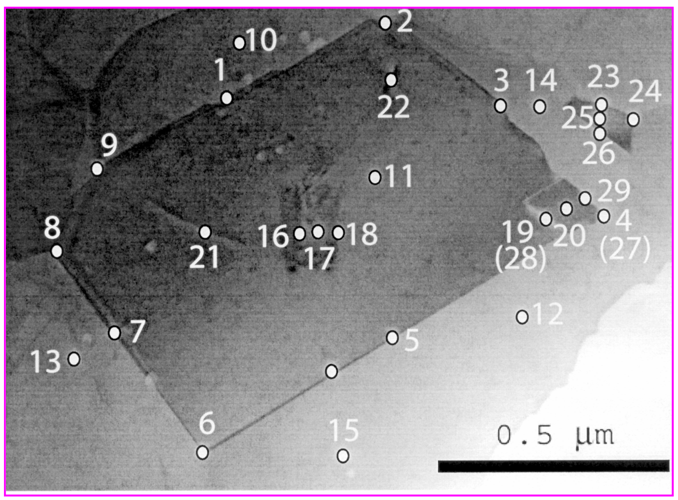
(110) epitaxial layer AFM image

Nanochemistry & Structure

Composition Variations

- EDS:
- Probe size ~ 1nm

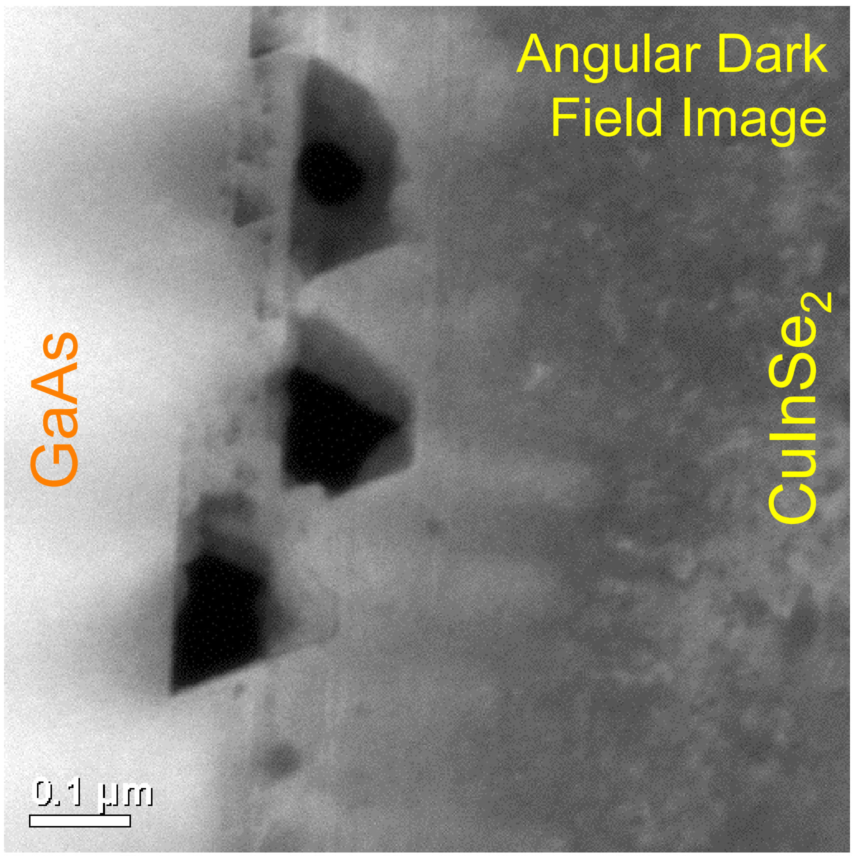




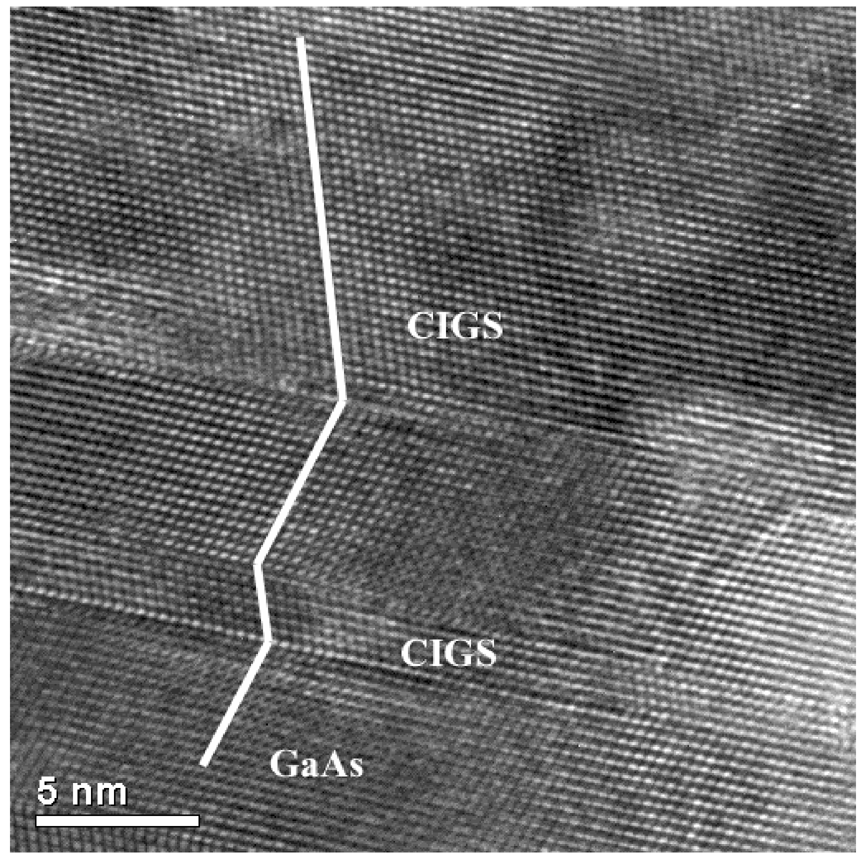
- Noisy data
- No obvious grain boundary change
- Data generally follows the tie line

CIS/GaAs Epitaxy

Kirkendal Voids
w (112)Se facets

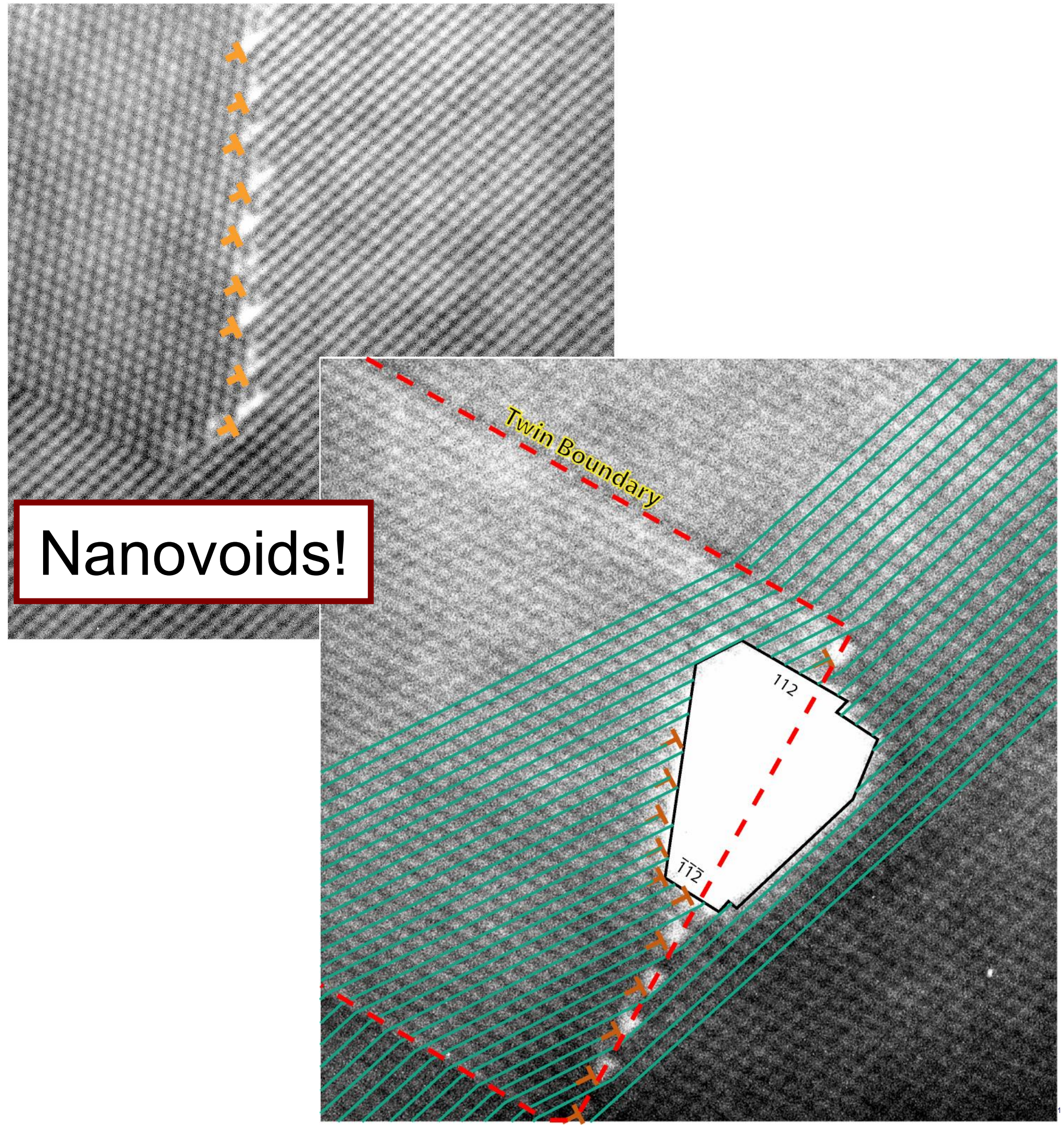


Stacking faults &
twins at interface



Voids

- From surface data we know faceting is common.
- Voids between grains in polycrystals.
- Voids within grains at twin terminations and dislocations.



Nanovoids!

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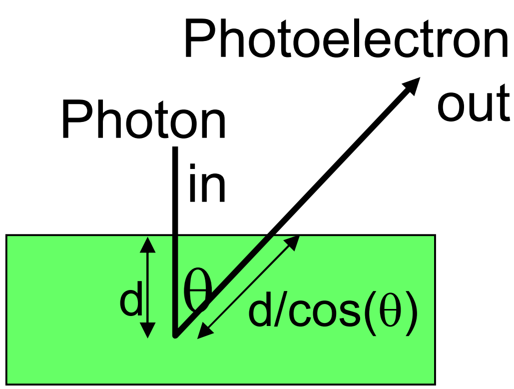
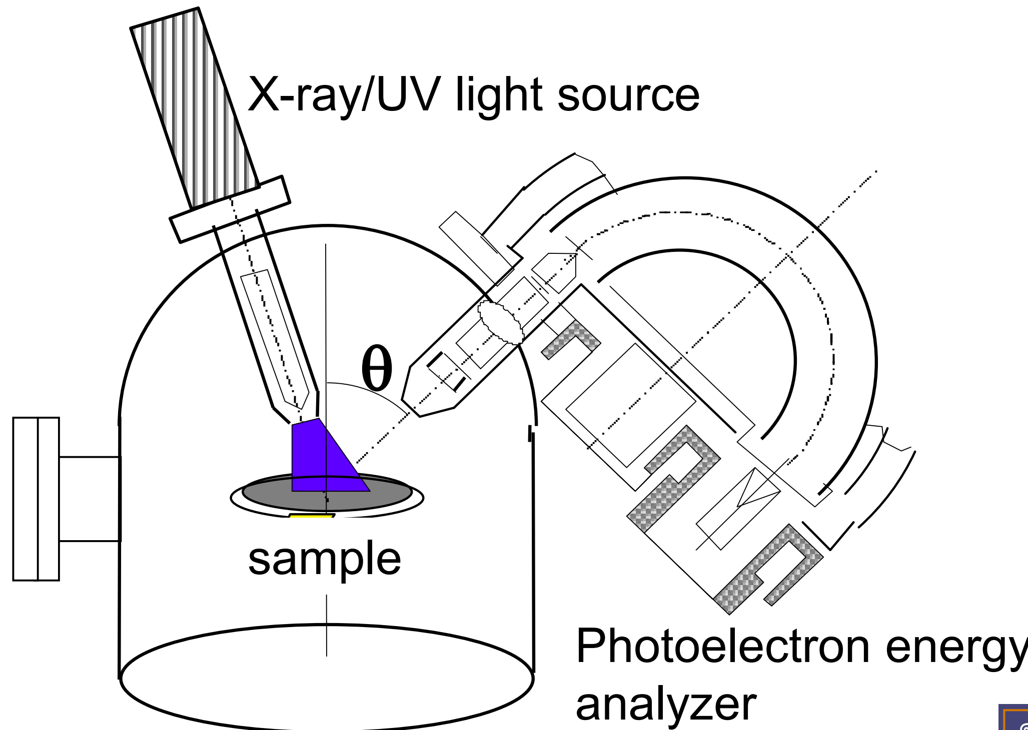
Surface Chemistry

CIGS Surface Chemistry

- Use very smooth (112) surfaces to study chemistry by angle-resolved photoelectron spectroscopy.



Angle θ controls probe depth



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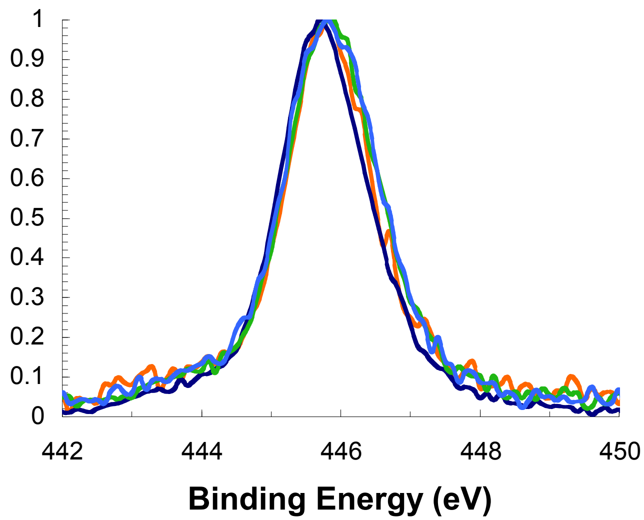
Angle-resolved Measurements

- No chemical shift between $(112)_{metal}$ and $(112)_{Se}$.



- No chemical shifts with photoelectron take-off angle

Oxidized surface is (In,Ga) oxide

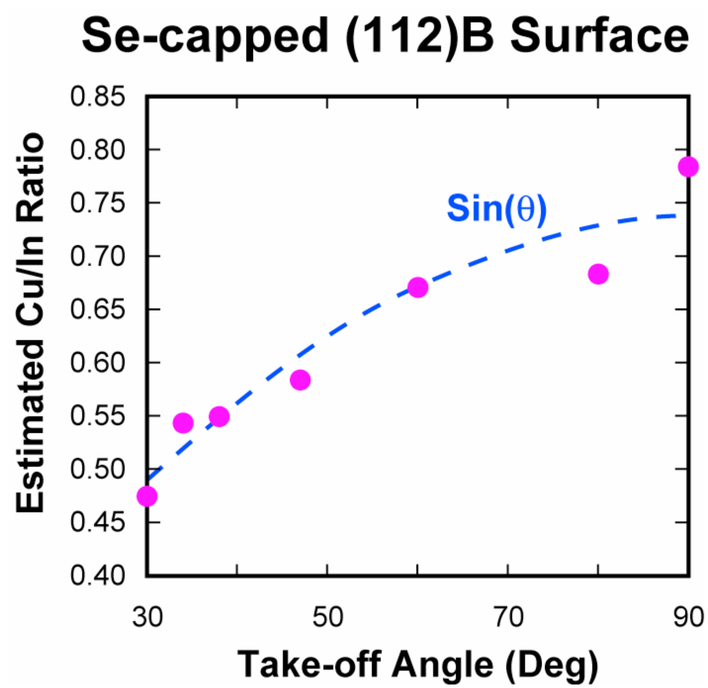
Angle-resolved Measurements

- Results show Cu-deficient Ga-rich surface

Cu	In	Ga	Se	O
0	0	28	6	66
0	37	0	0	63
18	16	0	6	60
24	16	10	50	0
24	16	10	50	0

Best fit by monolayer, at.%

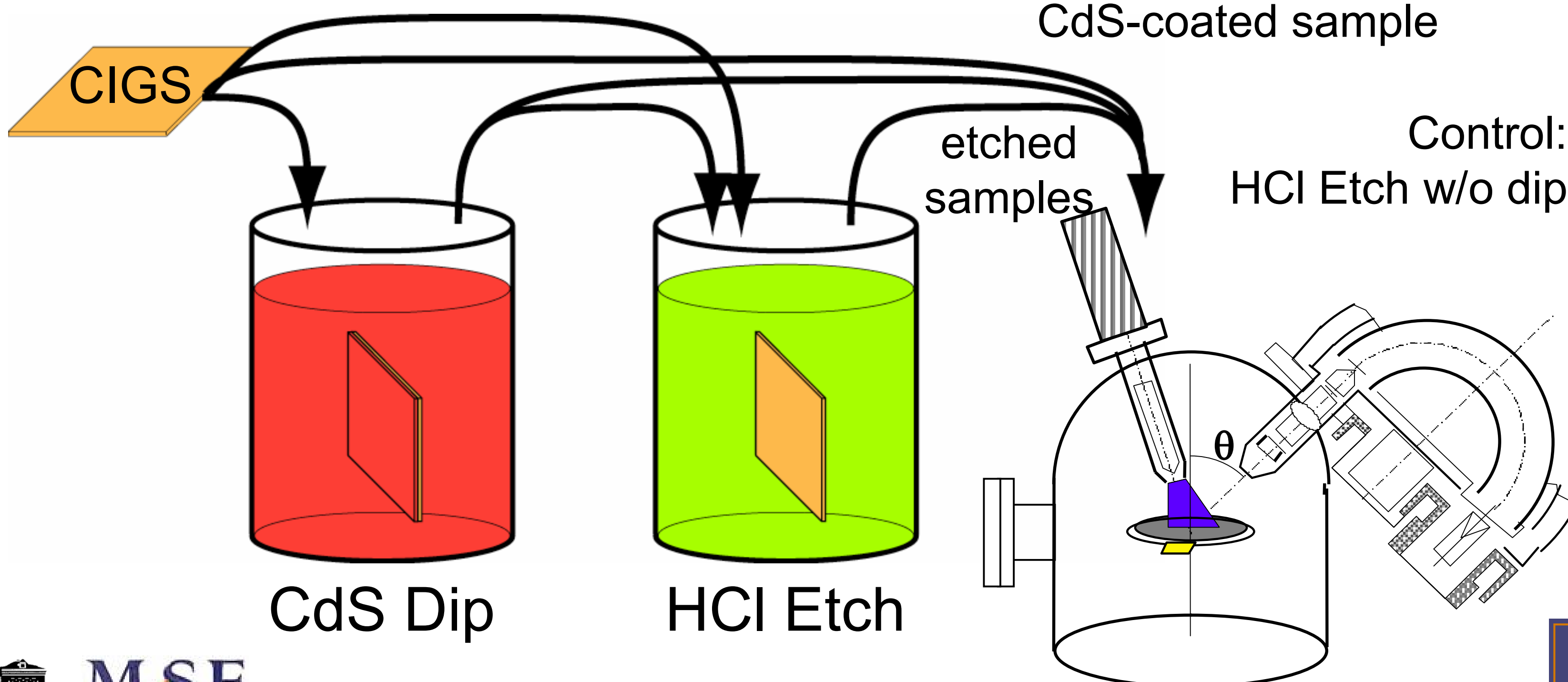
Air-exposed



Modelling suggests 1-2 monolayers with altered Cu-poor composition

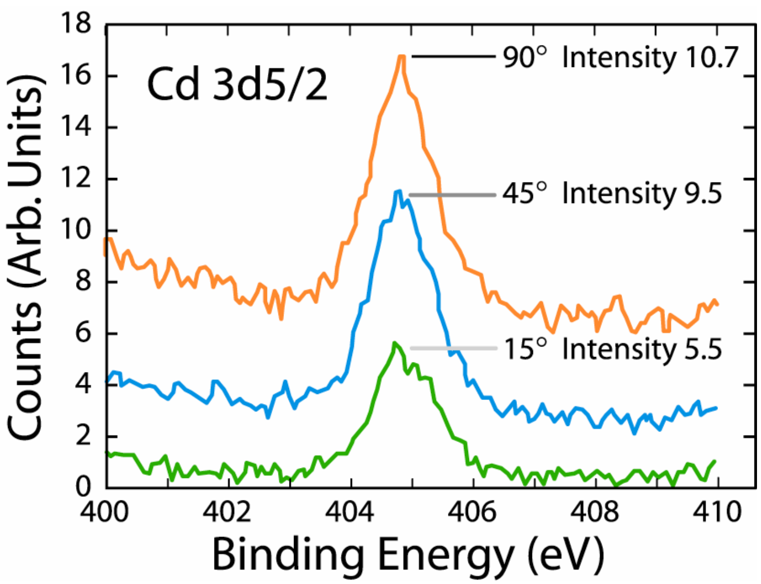
The CdS Heterojuction

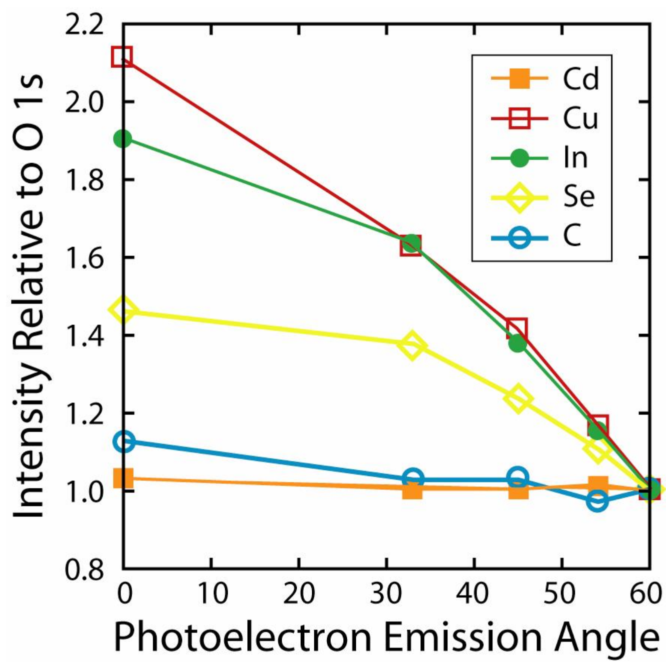
- The best CIGS solar cells have a heterojunction made by dip-coating CdS onto the CIGS.
- Plan: Use AR-PES to study the effect of the dip-coating bath on the surface.



CdS Dip Coating Results

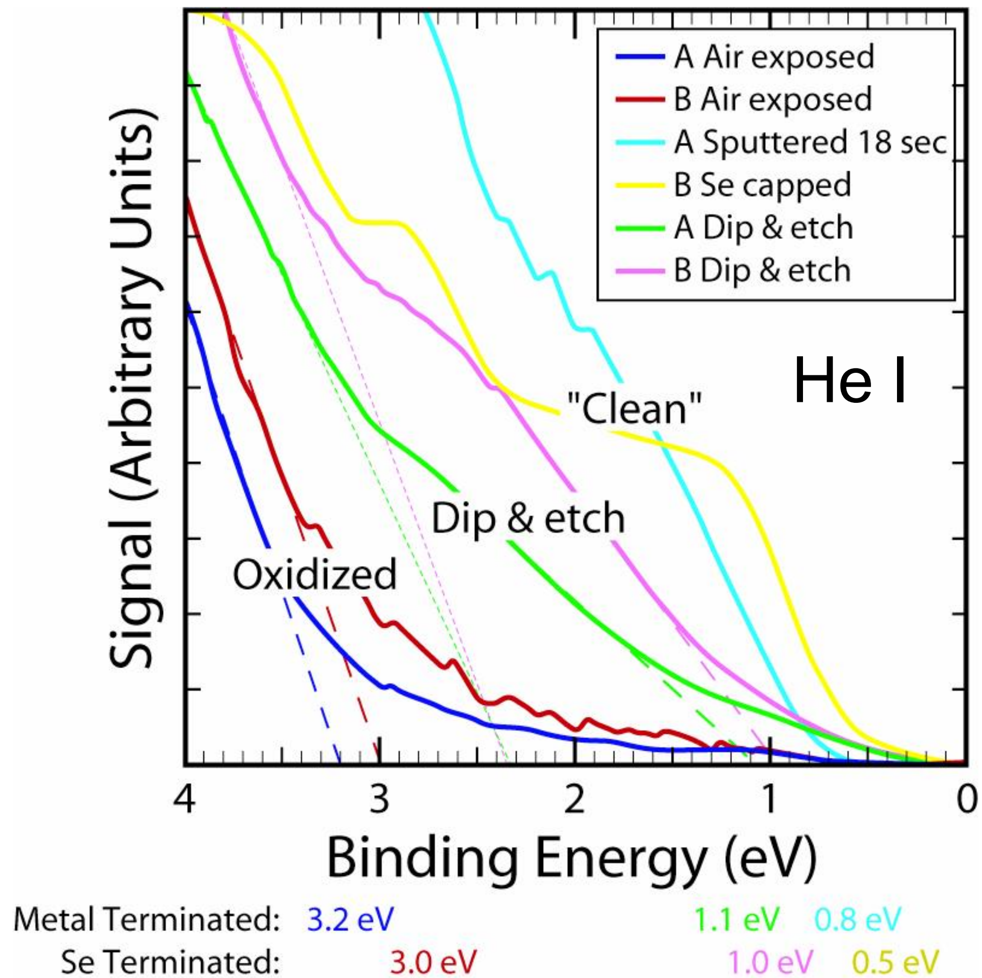
- Results show ~0.7 cation monolayers of Cd atoms in the first one (or two) atomic layers of the surface after etching.
- Fermi-edge shifts but core levels similar to sputtered & Se-capped samples.





CdS Dip Coating Results

- Comparison of valence bands
- Metal-terminated has ~0.2 eV higher binding energy
- Dip & etch samples have component with ~1eV edge.



The oxidized surfaces have a minority component (1%) consistent with the sputtered edge

Conclusions

- Copper chalcogenides are fascinating and unique materials.
- Defects dominate the optoelectronic properties.
- Growth mechanisms are unique and interesting.
- Thanks again to everyone who helped with this research, funded it, discussed results with me, and to you for listening!