Diffusion in $Cu(In,Ga)Se_2$ Photovoltaic Absorber Formation

Woo Kyoung Kim[1,3], J. Y. Shen[2], and T.J. Anderson[3]

[1] Institute of Energy Conversion, University of Delaware, USA
[2] General Research Institute for Non-ferrous Metals of Beijing, China
[3] Department of Chemical Engineering, University of Florida, USA

Outline

- $Cu(In,Ga)Se_2$ photovoltaics overview
- Diffusion reaction study using in-situ HT-XRD
  - ➔ CuSe/GaSe → $CuGaSe_2$
  - ➔ Cu-In + Se → $CuInSe_2$
- Preliminary study of DICTRA diffusion modeling
  - ➔ Cu-In + Se → $CuInSe_2$
- Summary

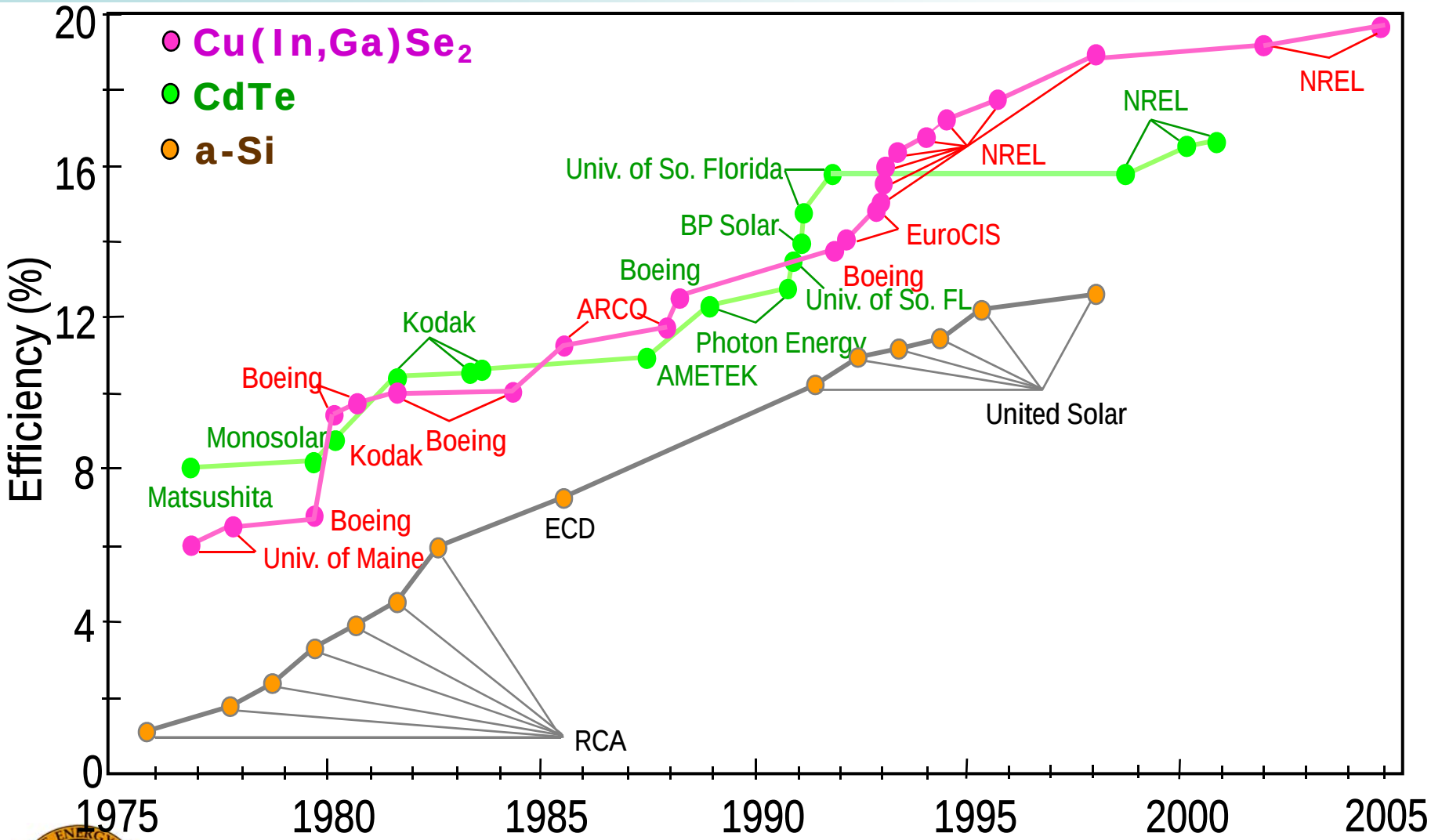
Thin Film CIGS Solar Cells

Building-integrated CIGS, 85kW Shell Solar

GLOBAL SOLAR
Systems That Deliver

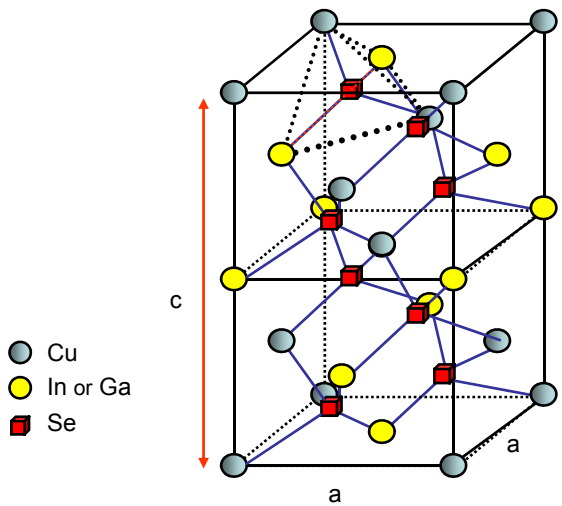
Flexible, lightweight $Cu(InGa)Se_2$ - Global Solar

Best Efficiency of Thin Film Cells

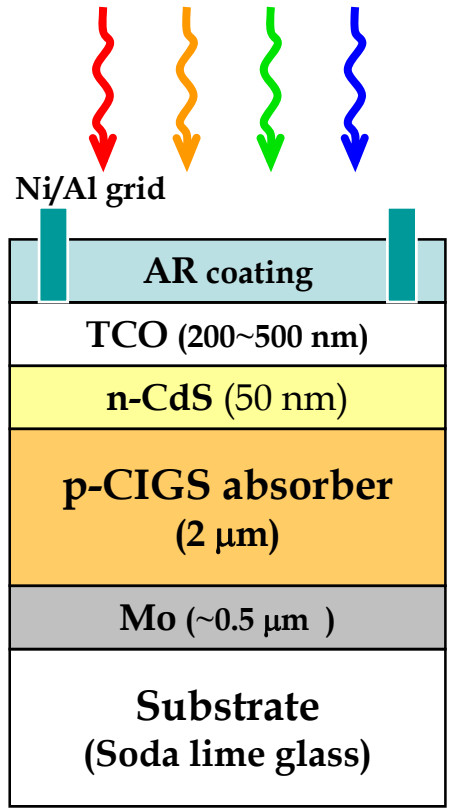


$Cu(In,Ga)Se_2$ Solar Cells

- **Most promising thin film photovoltaic material**
  - → η = 19.9 %, NREL (2008)
  - → Direct band gap
    : band gap engineering (E_g ~ 1.2 eV at x(Ga)=0.3)
  - → High optical absorption coefficient
    : thin film ~ 2 μm
  - → High radiation resistance
  - → High reliability



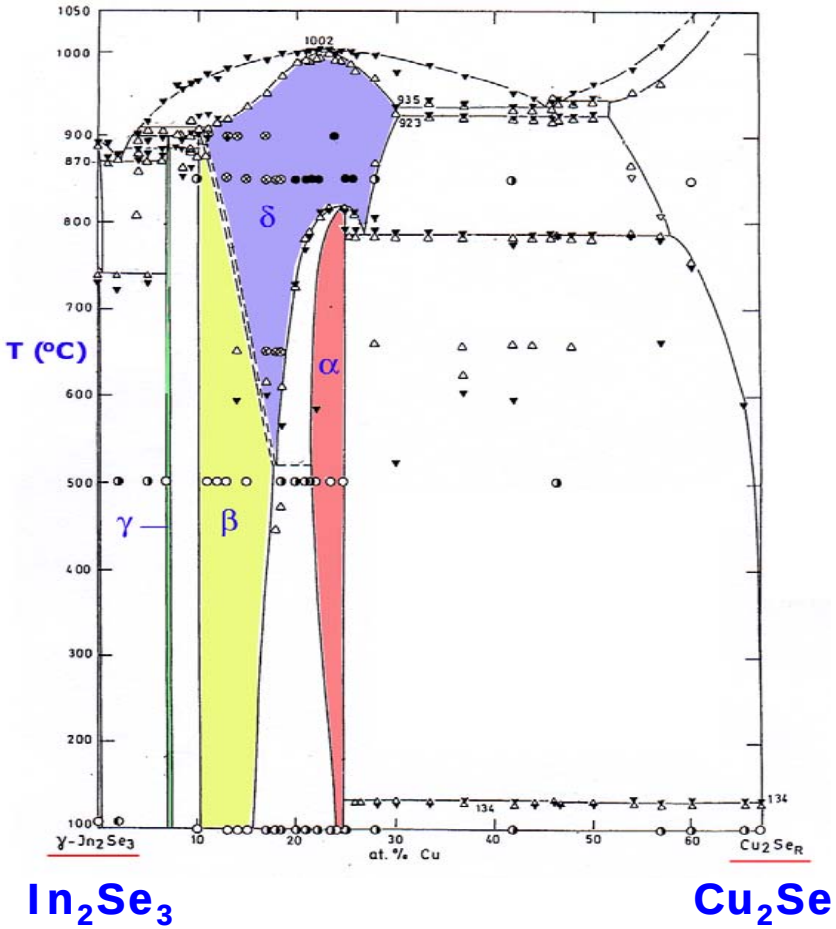
Chalcopyrite CIGS structure



Typical device structure

Cu-In-Se Phase Equilibrium

Cu_2Se-In_2Se_3 pseudo-binary



In_2Se_3 **Cu_2Se**

Wide composition tolerance of chalcopyrite α-$CuInSe_2$

x(Cu) = 21~25 at.%

δ : $CuInSe_2$ – *sphalerite*

β : $CuIn_3Se_5$ – *ODC*

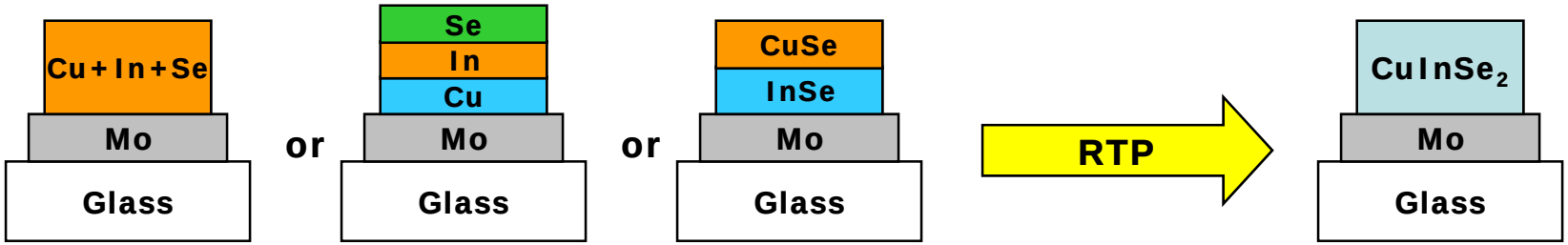
γ : $CuIn_5Se_8$ – *ODC*

T. Gödecke et al., Z. Metallkd (2000)

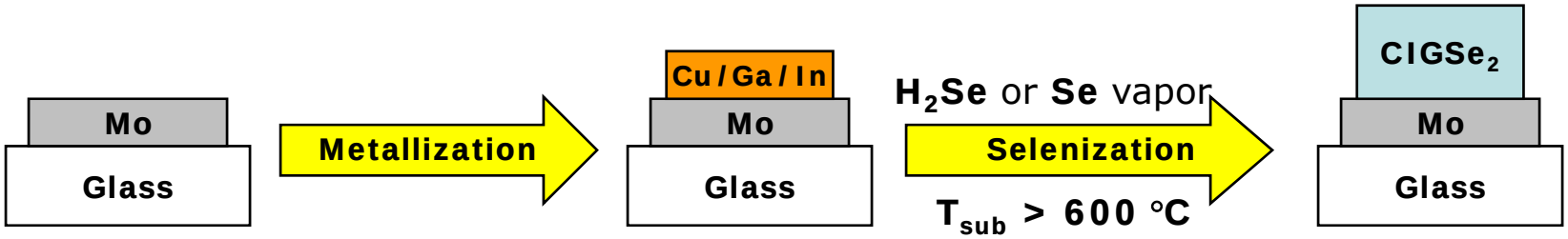
Common Deposition Techniques

- Co-evaporation of elements (PVD, MBE etc.)
  : Cu, In, Ga, Se
  → ***Highest efficiency !!***

- Rapid thermal process (RTP) of stacked or elemental precursors

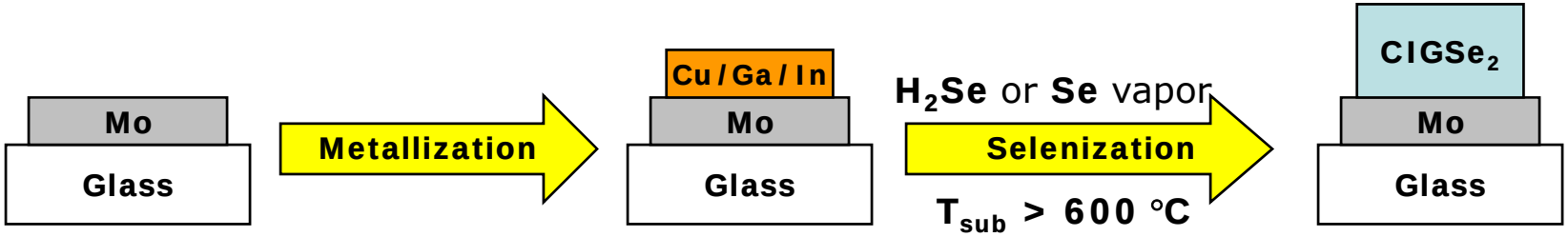


- Selenization of metallic precursors: ***"Shell Solar" 2 step method***



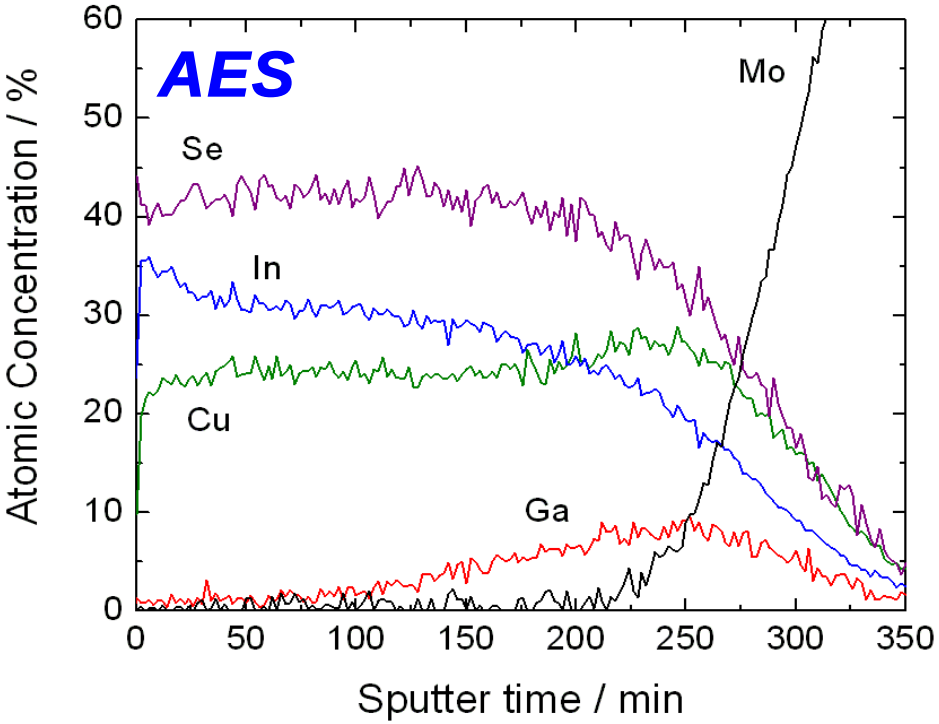
Diffusion Issues

- Selenization of metallic precursors: ***"Shell Solar" 2 step method***



Ga accumulation at back !

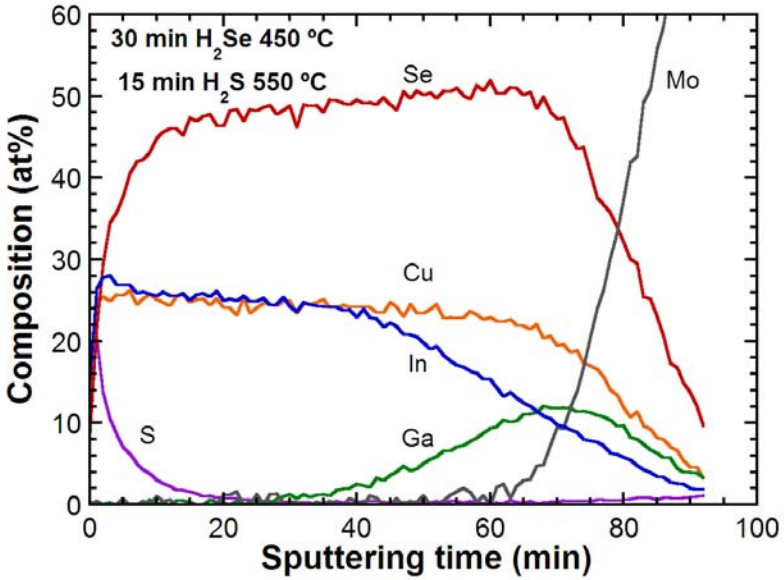
Decrease device performance !



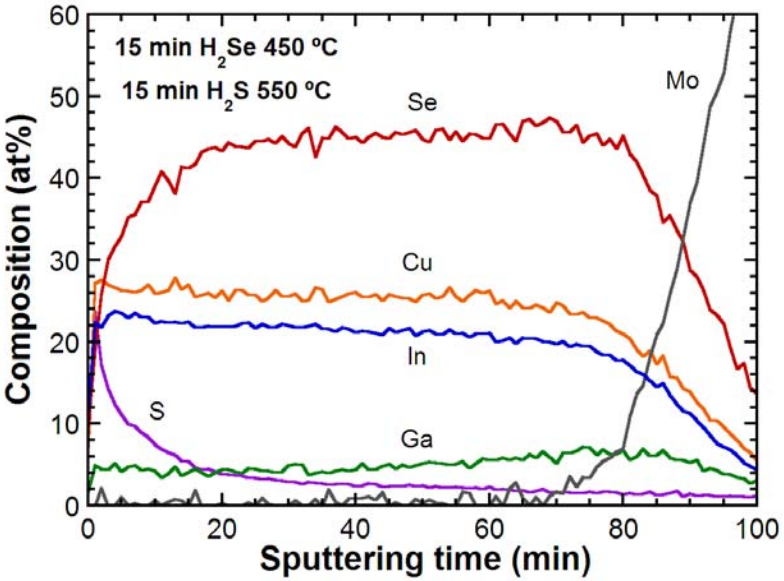
Diffusion Issues

Cu-Ga-In/Mo $\xrightarrow{H_2Se\ /\ H_2S}$ $Cu(In,Ga)(Se,S)_2/Mo$

Complete H_2Se reaction *prior to H_2S*
Ga *segregated to back*



Partial H_2Se reaction *prior to H_2S*
Ga *distributed through film*



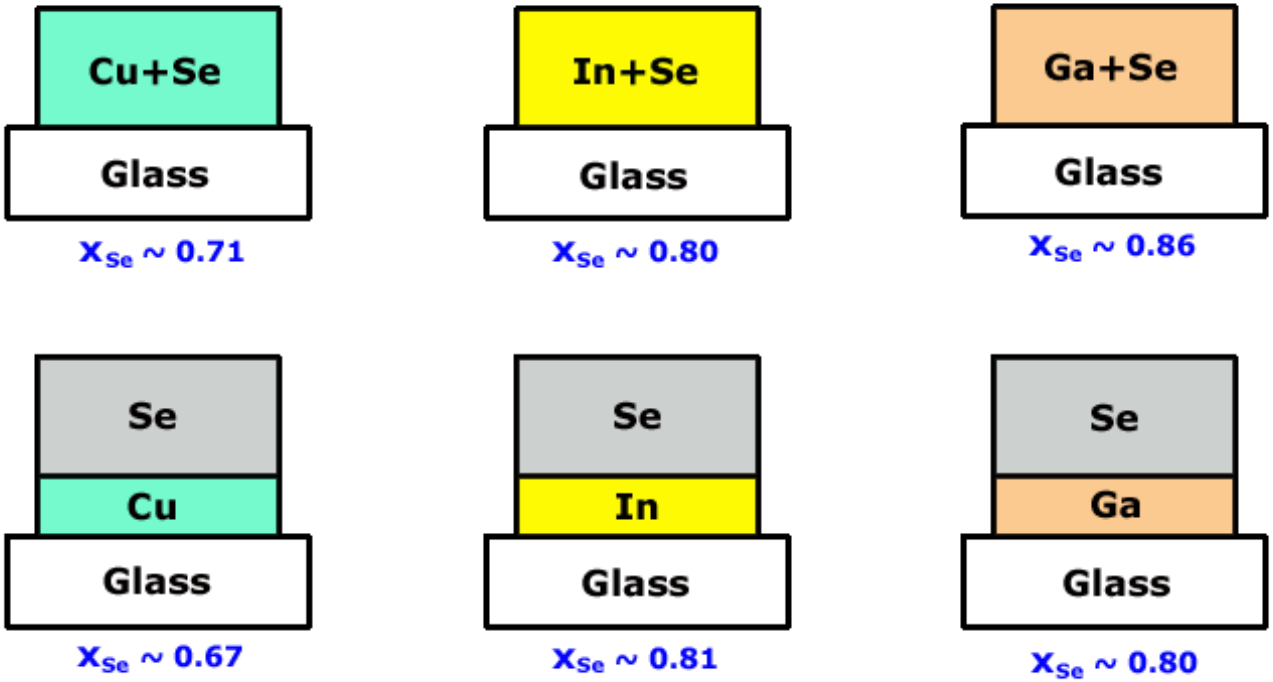
G. Hanket, W. Shafarman, R. Birkmire. , Proc. 4th World Conf. on PVEC (2006).

Reaction pathways and kinetics using *in-situ* HT-XRD

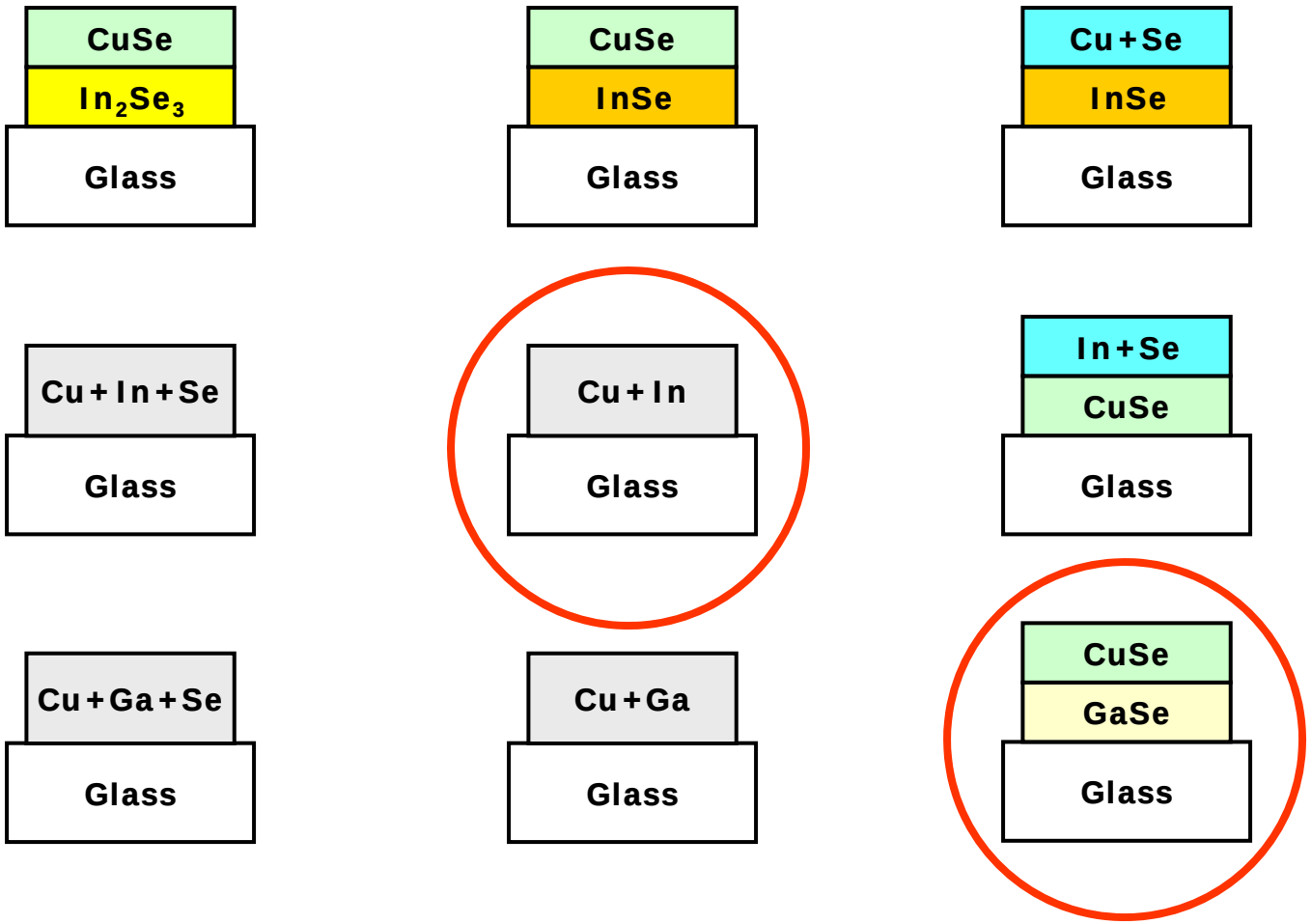
Institute of Energy Conversion
University of Delaware

NIST Diffusion Workshop
May 12, 2008

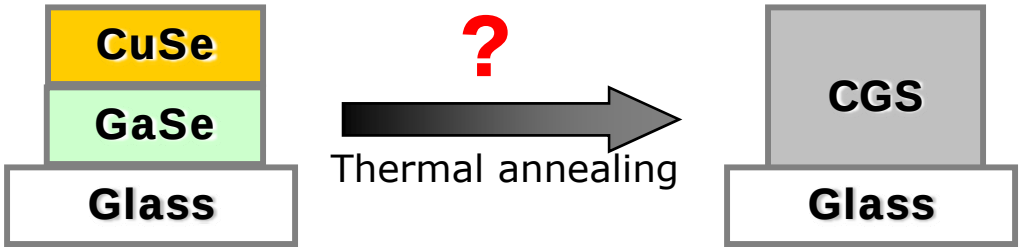
Precursor Diffusion Couples



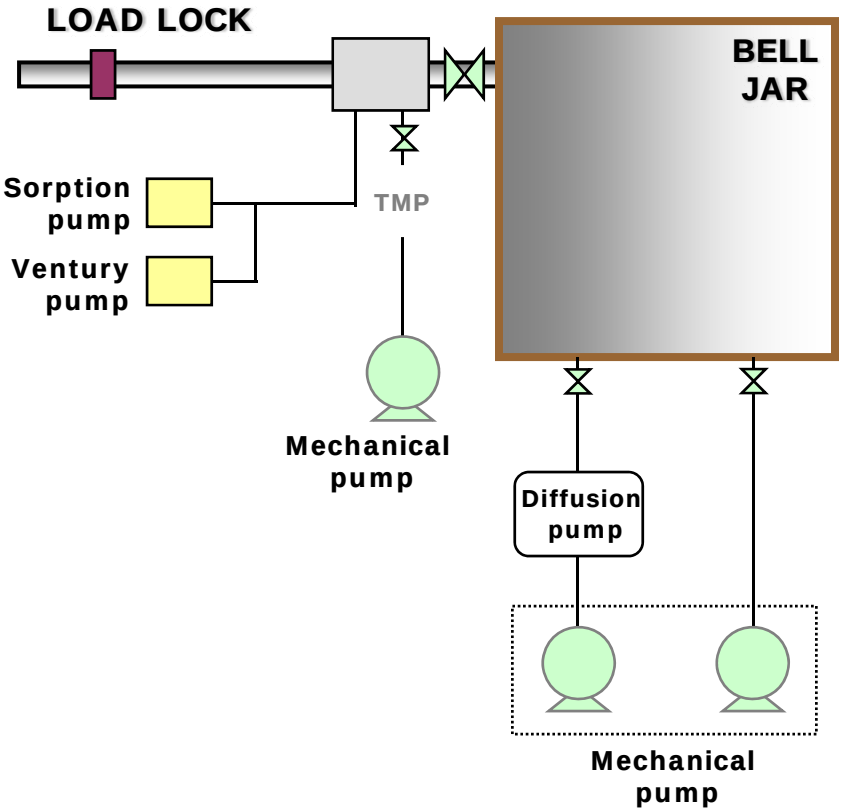
Precursor Diffusion Couples



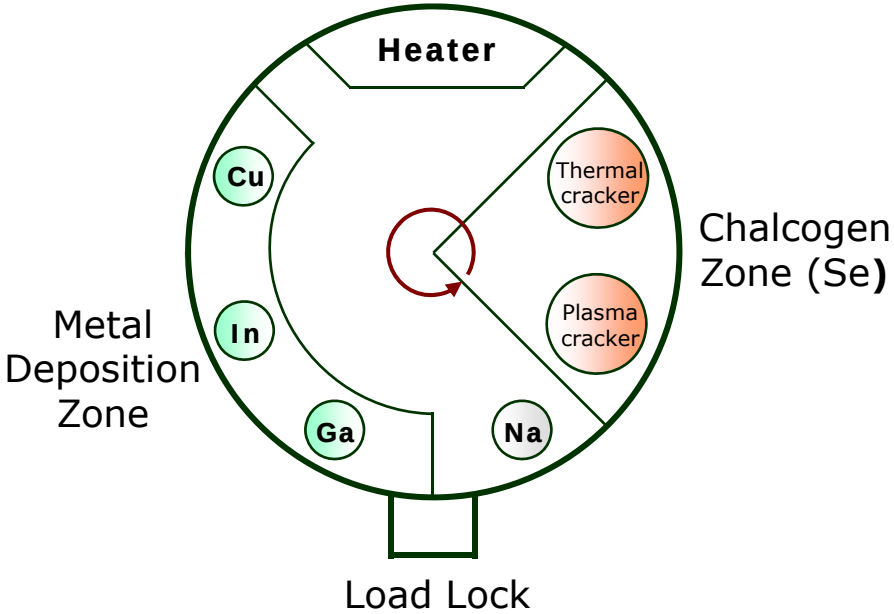
$CuGaSe_2$ formation from a bilayer GaSe/CuSe diffusion couple



Precursor Preparation by MEE System



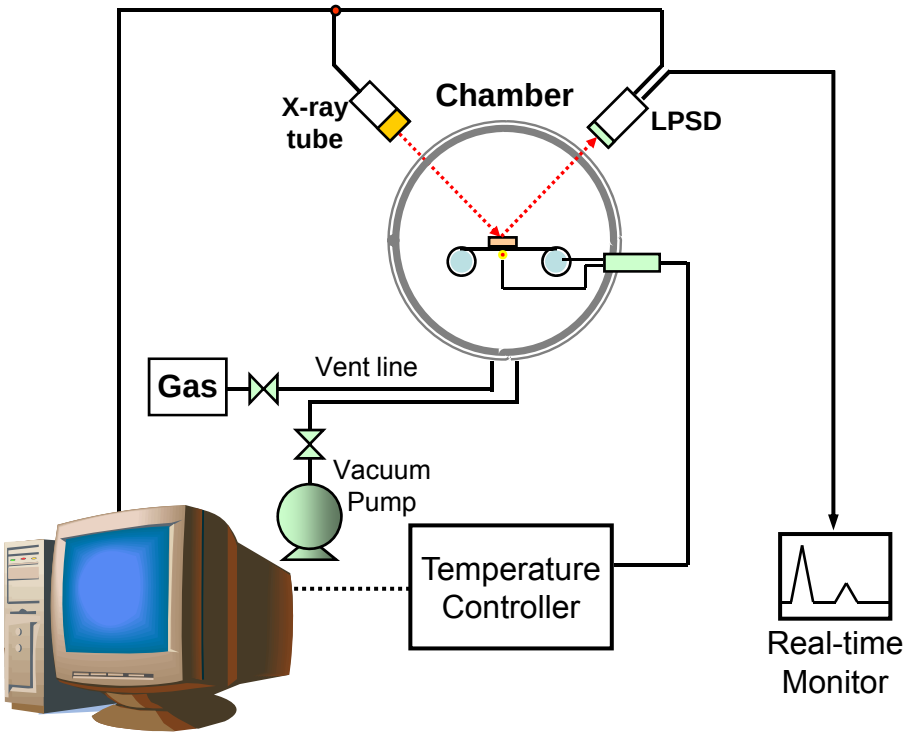
Schematic top view

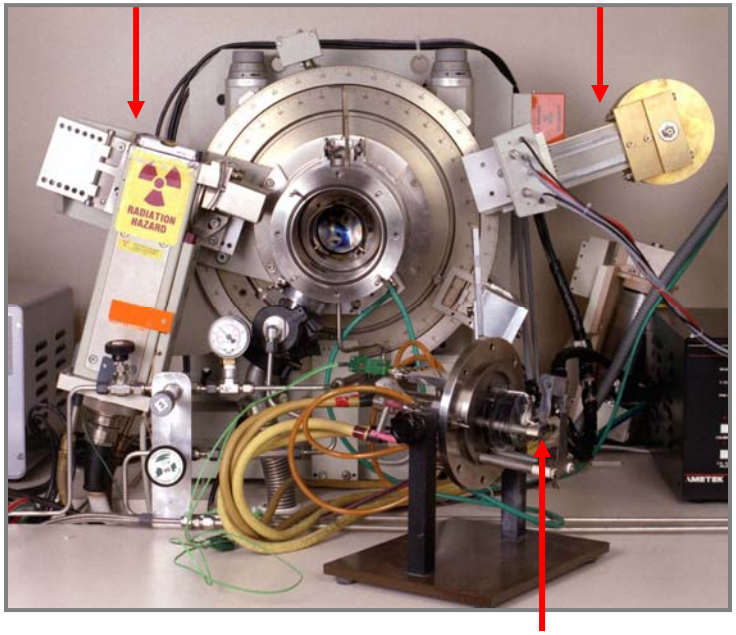


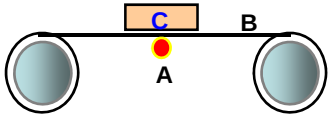
- ➔ Ultra high vacuum system
- ➔ Operating pressure : ~ 10^{-8} Torr

- ➔ Rotating platen with 9 substrates :2″×2″ square, 2″ circular
- ➔ Sequential deposition :Heating → Cu → In → Ga → (Na) → Se

HT-XRD System



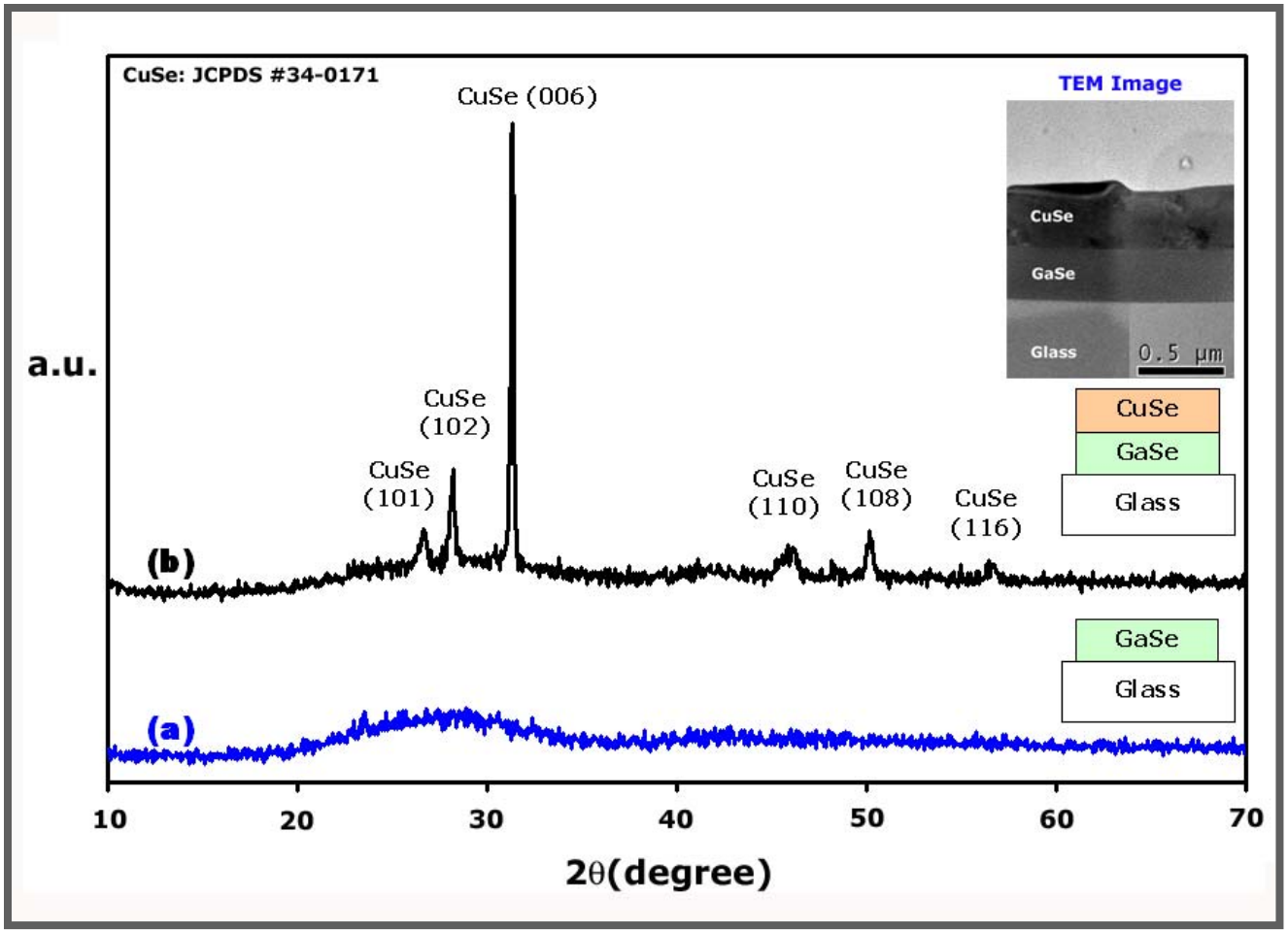




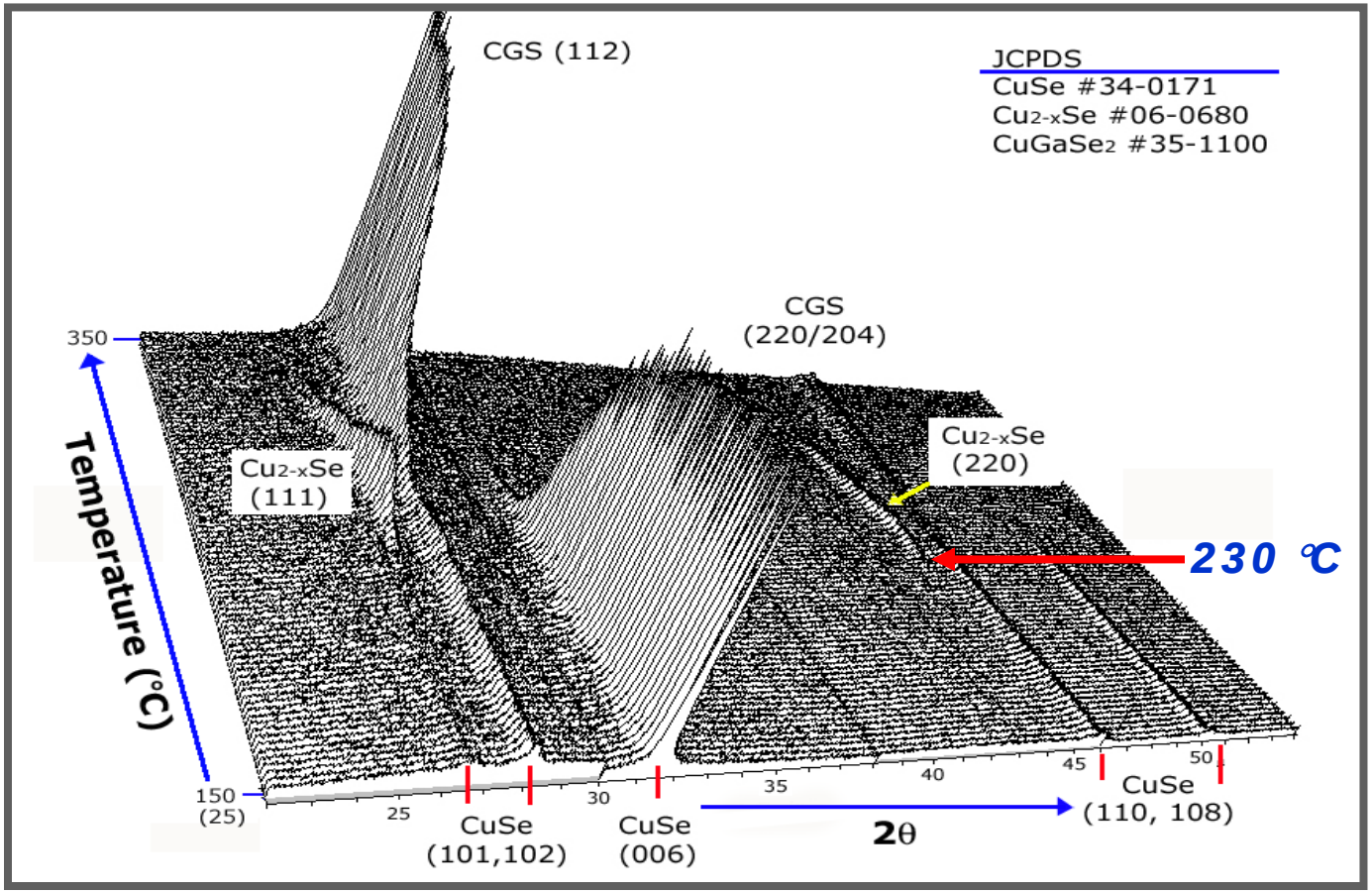
A: Spot-welded thermocouple
B: Heater strip (Pt20%Rh)
C: Sample

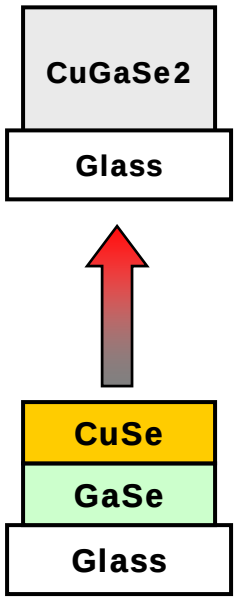
➔ ***High Temperature Materials Laboratory of Oak Ridge National Lab.***

Precursor Structure



Temperature ramp anneal





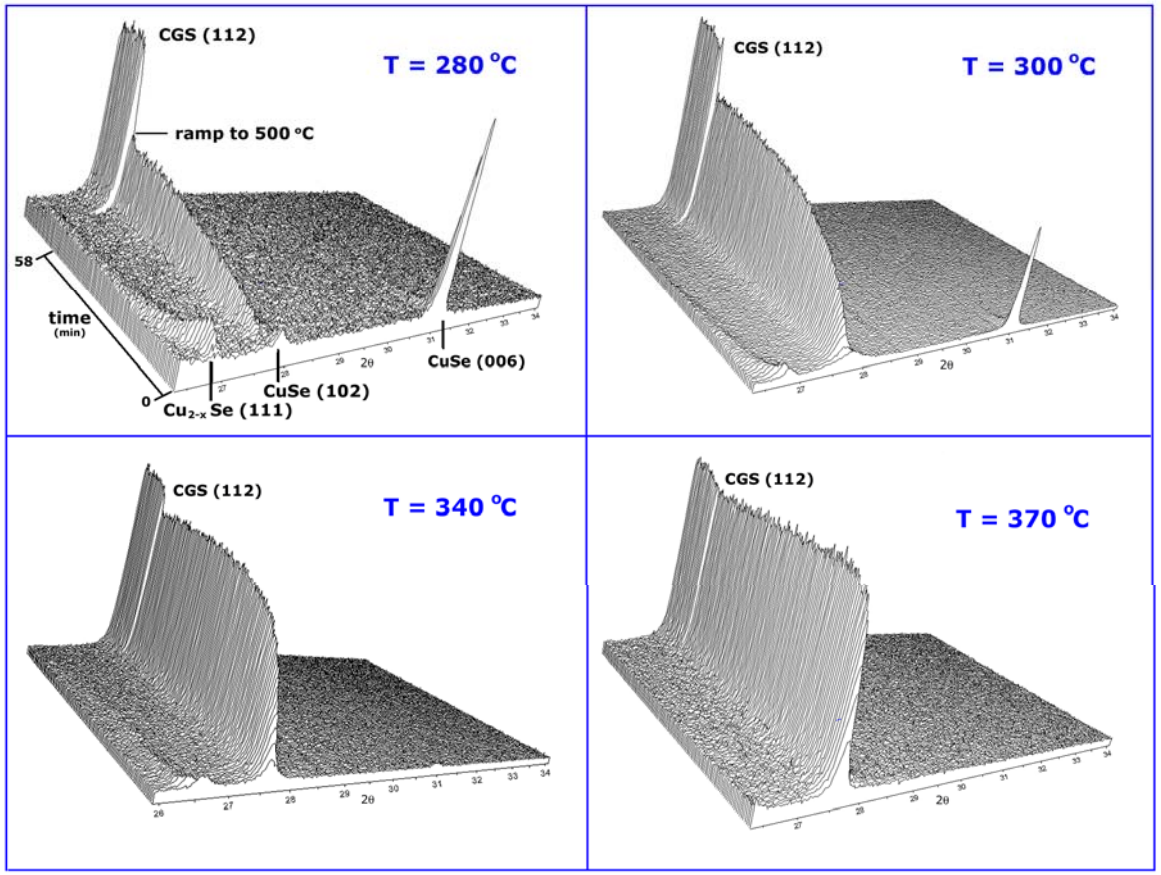
[Cu]/[Ga]=1.02

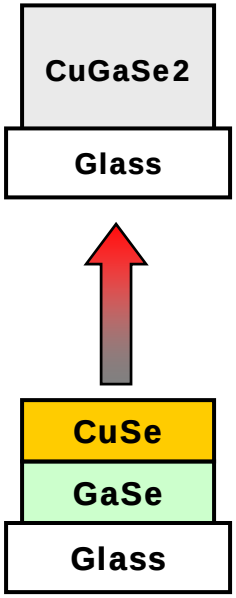
[Se]/[Cu+Ga]=0.97

$CuSe + GaSe \rightarrow Cu_{2-x}Se + Se + GaSe\ (or\ Ga_2Se_3) \rightarrow CuGaSe_2$

amorphous

Isothermal annealing





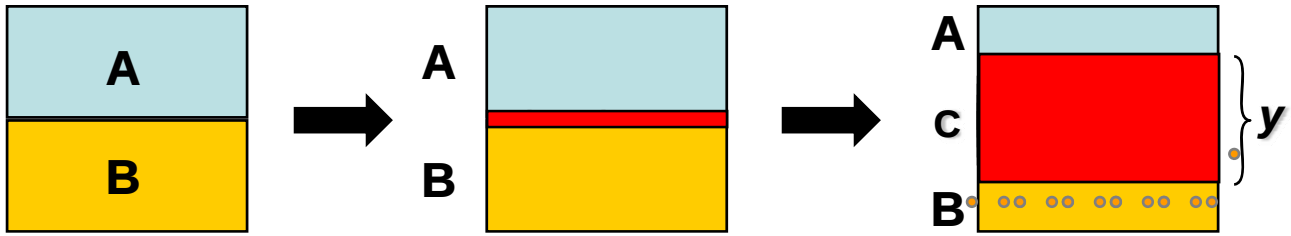
Assumption:

➔ Maximum peak area = 100 % reaction

➔ Normalized peak area = fractional reaction

Solid-state Growth Models

- **Parabolic growth model**



Before reaction

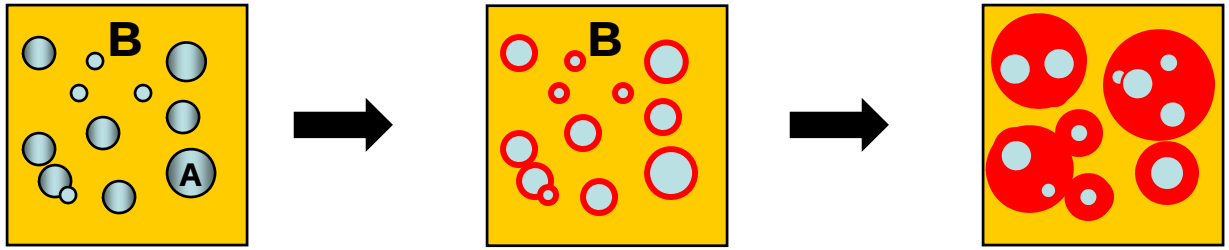
Nucleation at A-B interface

Diffusion thru product & reaction (ex. $D_{BC} > D_{AC}$)

$$\frac{dy}{dt} = \frac{D \cdot k}{y}$$

$$y^2 = k_p \cdot t$$

- **Avrami growth model**



Phase A Covered with B

Nucleation

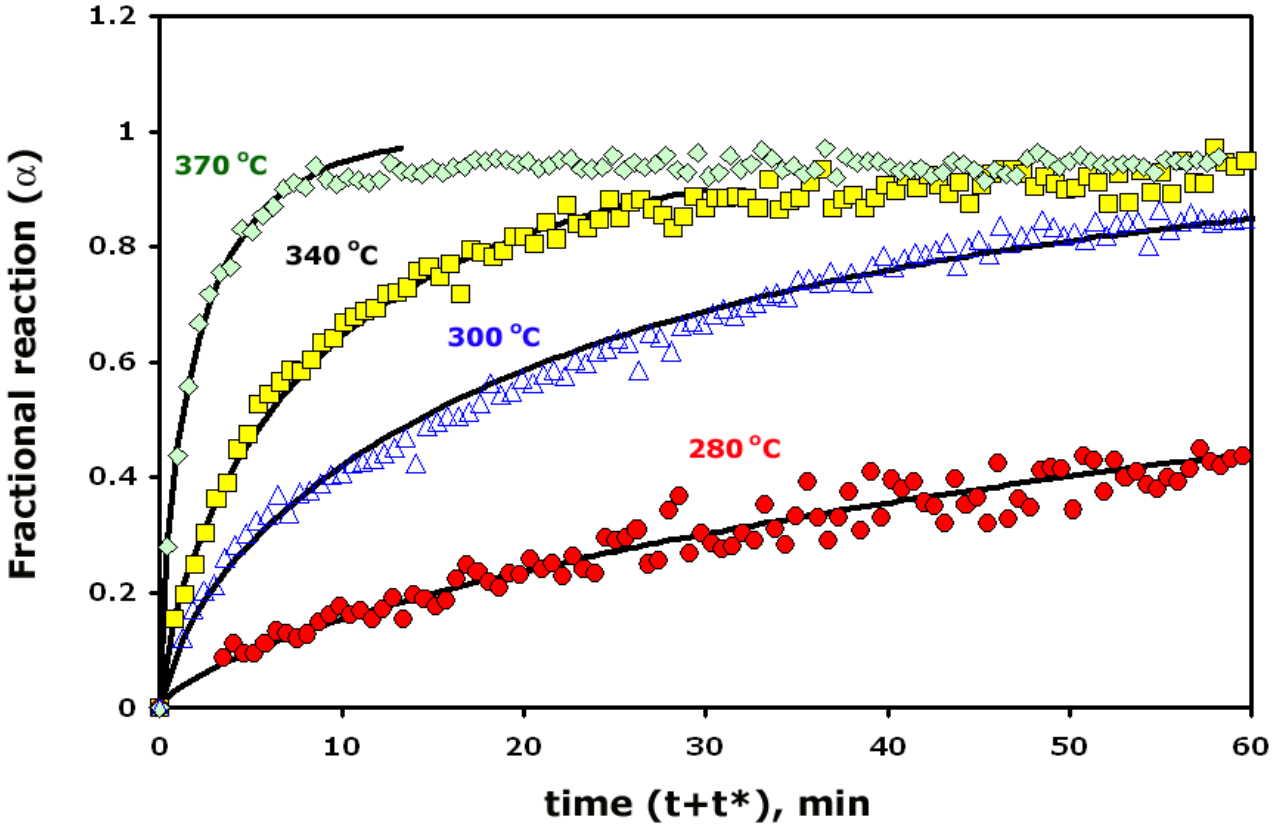
Diffusion & growth

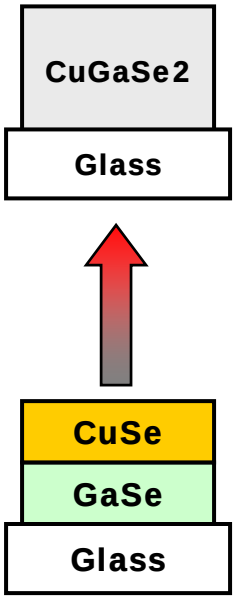
$$x = 1 - \exp[-(kt)^n]$$

$$\ln[-\ln(1-x)] = n\ln t + n\ln k$$

$0.5 < n < 1.5$
(1-D diffusion)

Modified Avrami Analysis

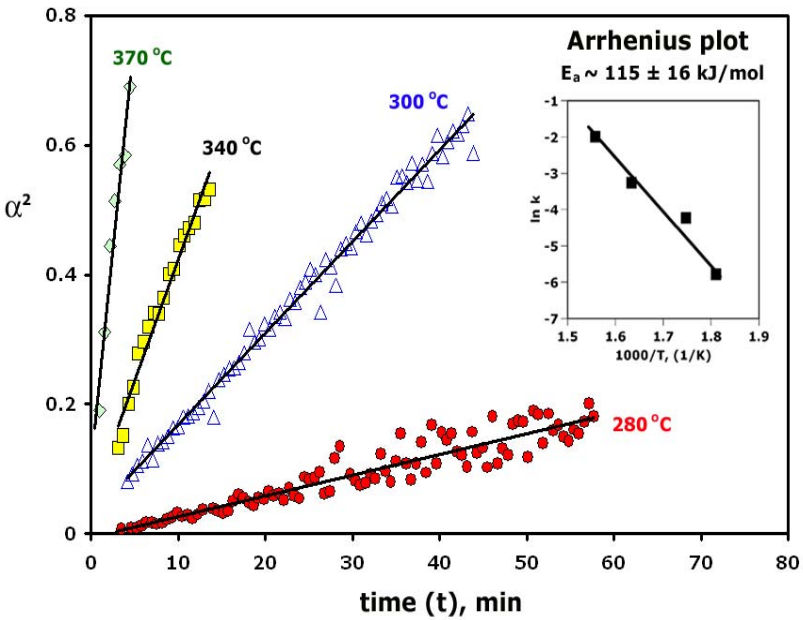




$$\alpha = 1 - \exp[-(k(t+t^*))^n]$$

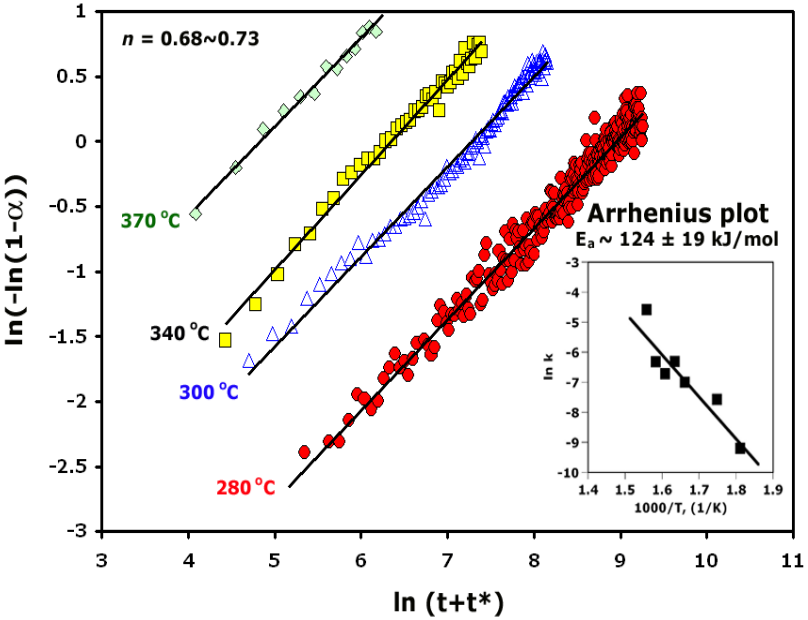
Kinetic Analysis

Parabolic model



$$\alpha^2 \sim k \cdot t$$

Modified Avrami model

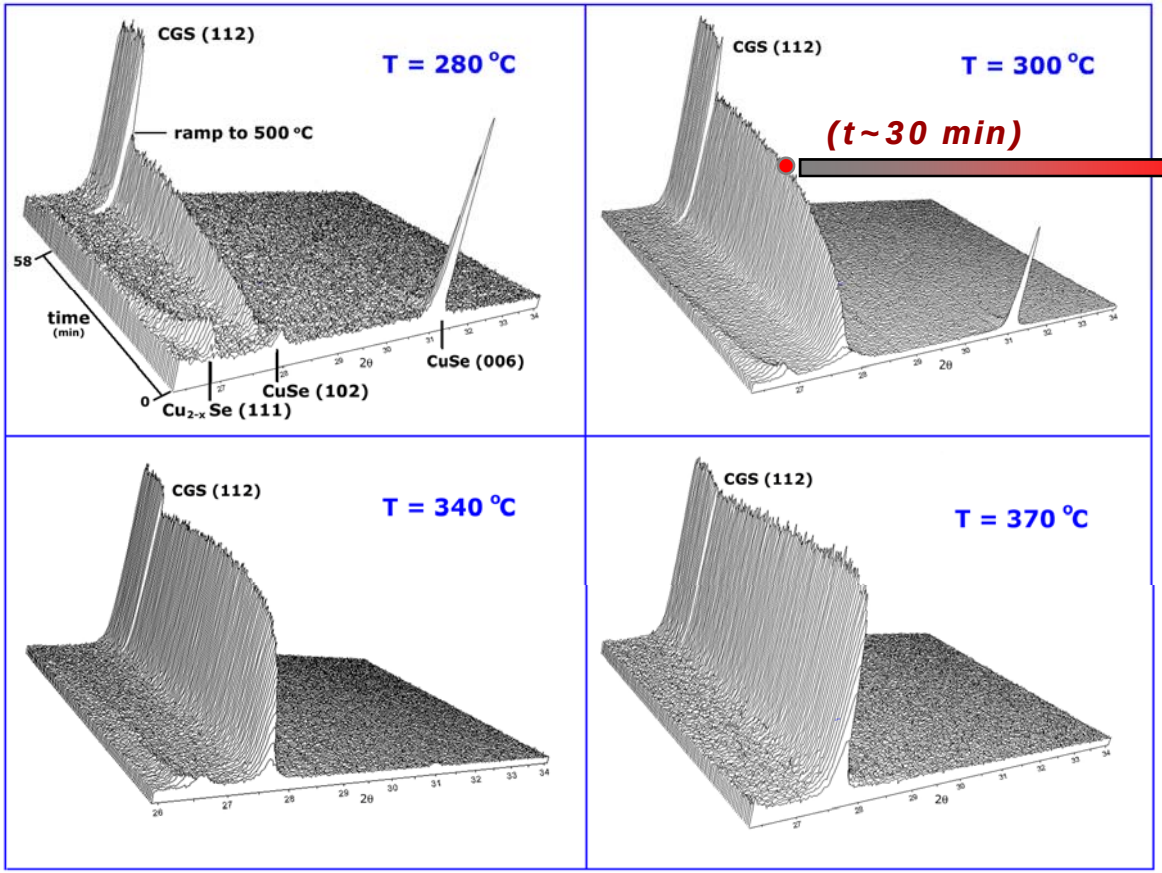


$$\ln[-\ln(1-\alpha)] = n\ln(t+t^*) + n\ln k$$

➔ *Analysis suggests one-dimensional diffusion controlled reaction*

TEM-EDS

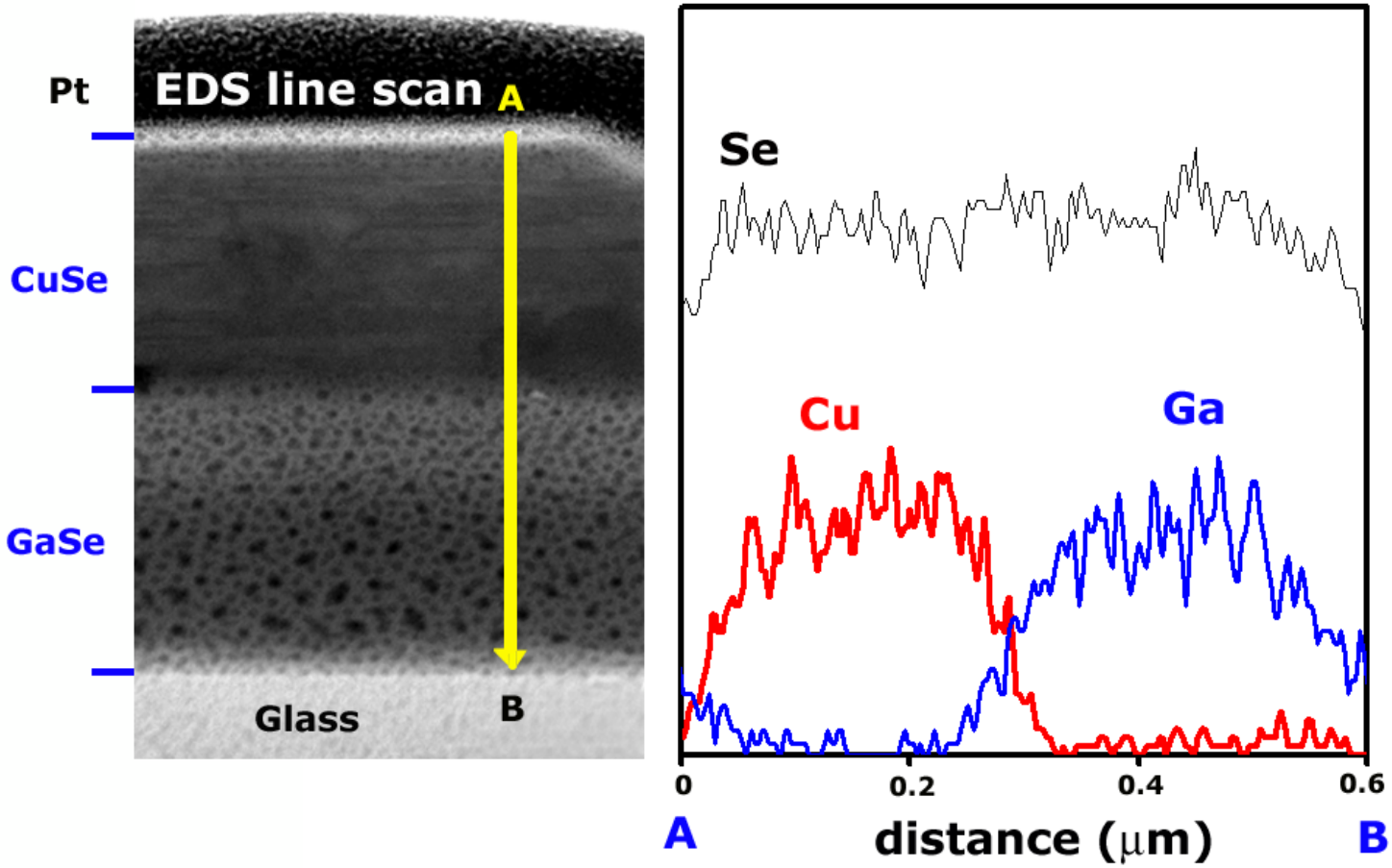
Isothermal annealing



TEM-EDS

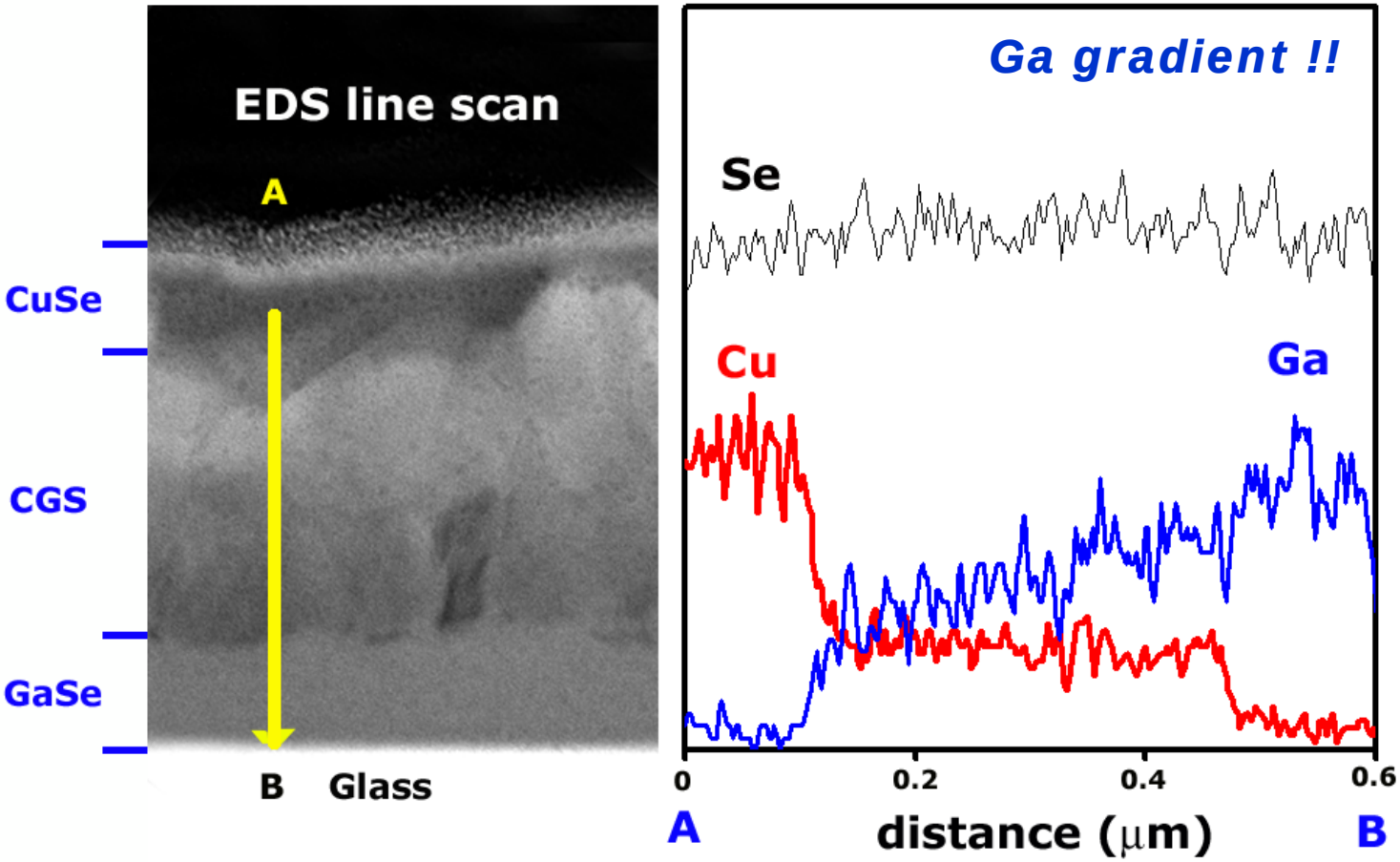
TEM-EDS Analysis

Glass / GaSe / CuSe Precursor

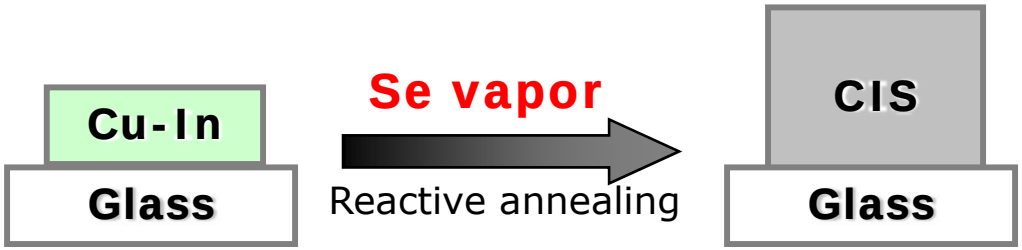


TEM-EDS Analysis

Glass / GaSe / CGS / CuSe annealed for 30 min, at 300 °C

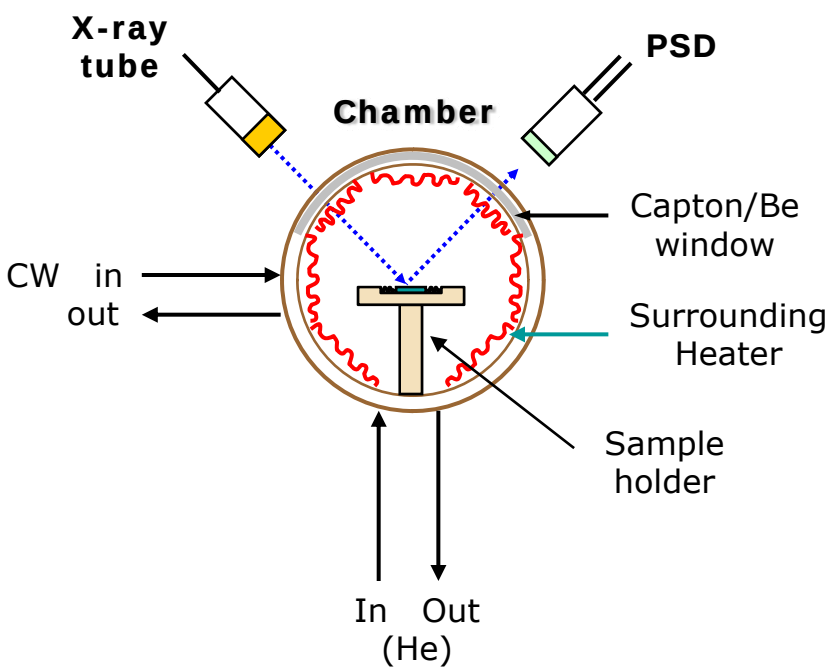


$CuInSe_2$ formation from selenization of Cu-In precursor

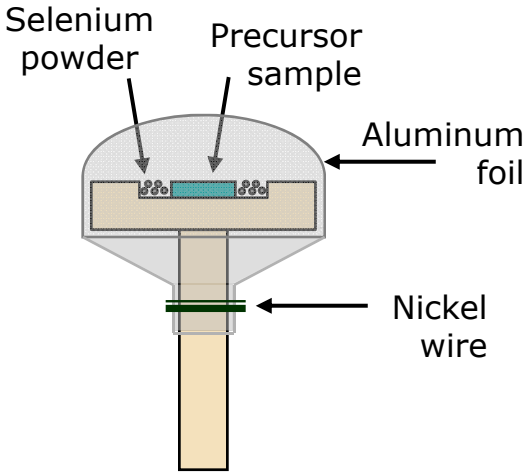


HT-XRD with Selenization Chamber

Panalytical Philips X'pert system



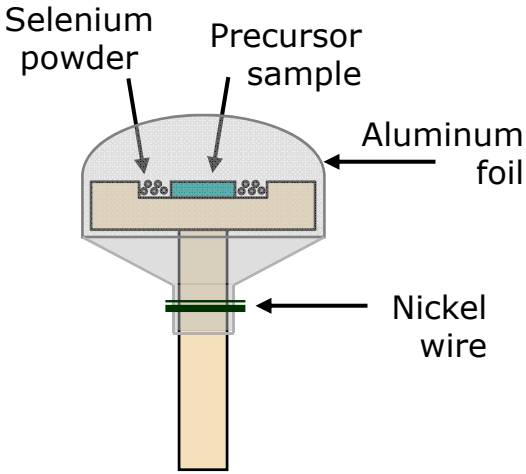
Sample holder



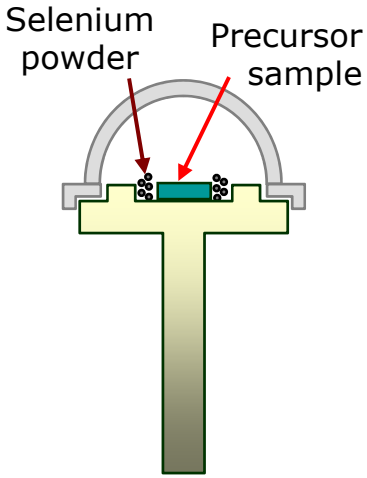
➔ ***High Temperature Materials Laboratory, ORNL***

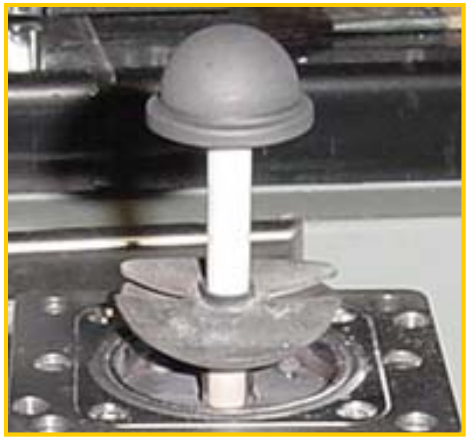
Selenization Chamber

Aluminum foil



Graphite dome

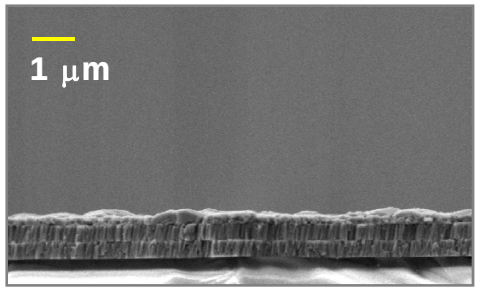




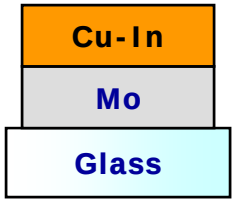
- **Al foil :**
  - **(1) Loss of X-ray intensity**
  - **(2) Possible reaction with Se above 650°C**
- **Graphite dome :**
  - **(1) Easy to handle**
  - **(2) Extremely X-ray transparent**
  - **(3) High stability**

SEM / EPMA

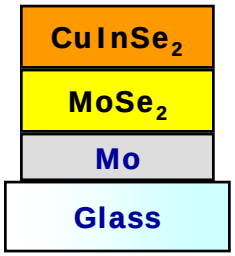
Precursor



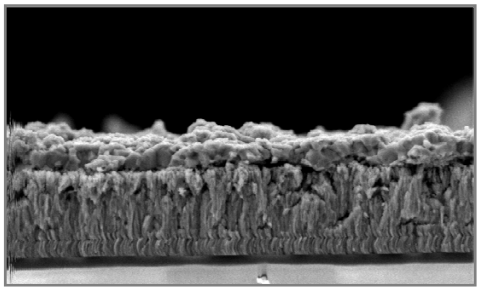
$\frac{[Cu]}{[In]} \sim 1.0$

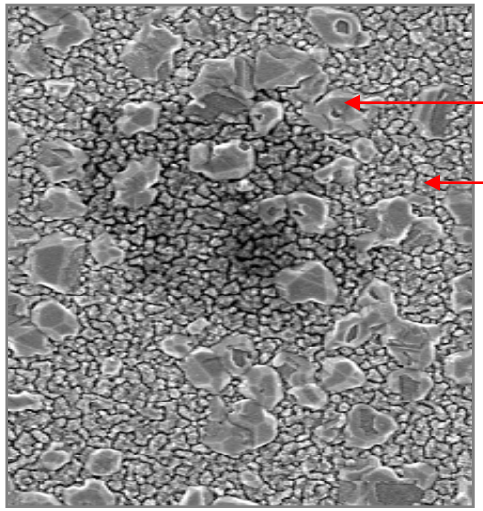


Selenization



Selenized CIS





Island (In-rich)

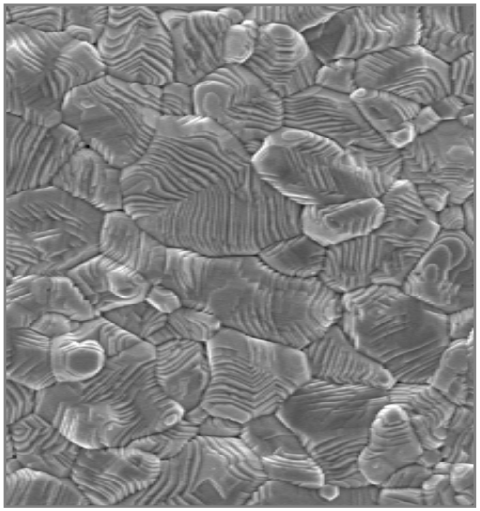
Matrix (Cu_2In+ CuIn)

1 μm

EPMA Results (Va=6 keV)

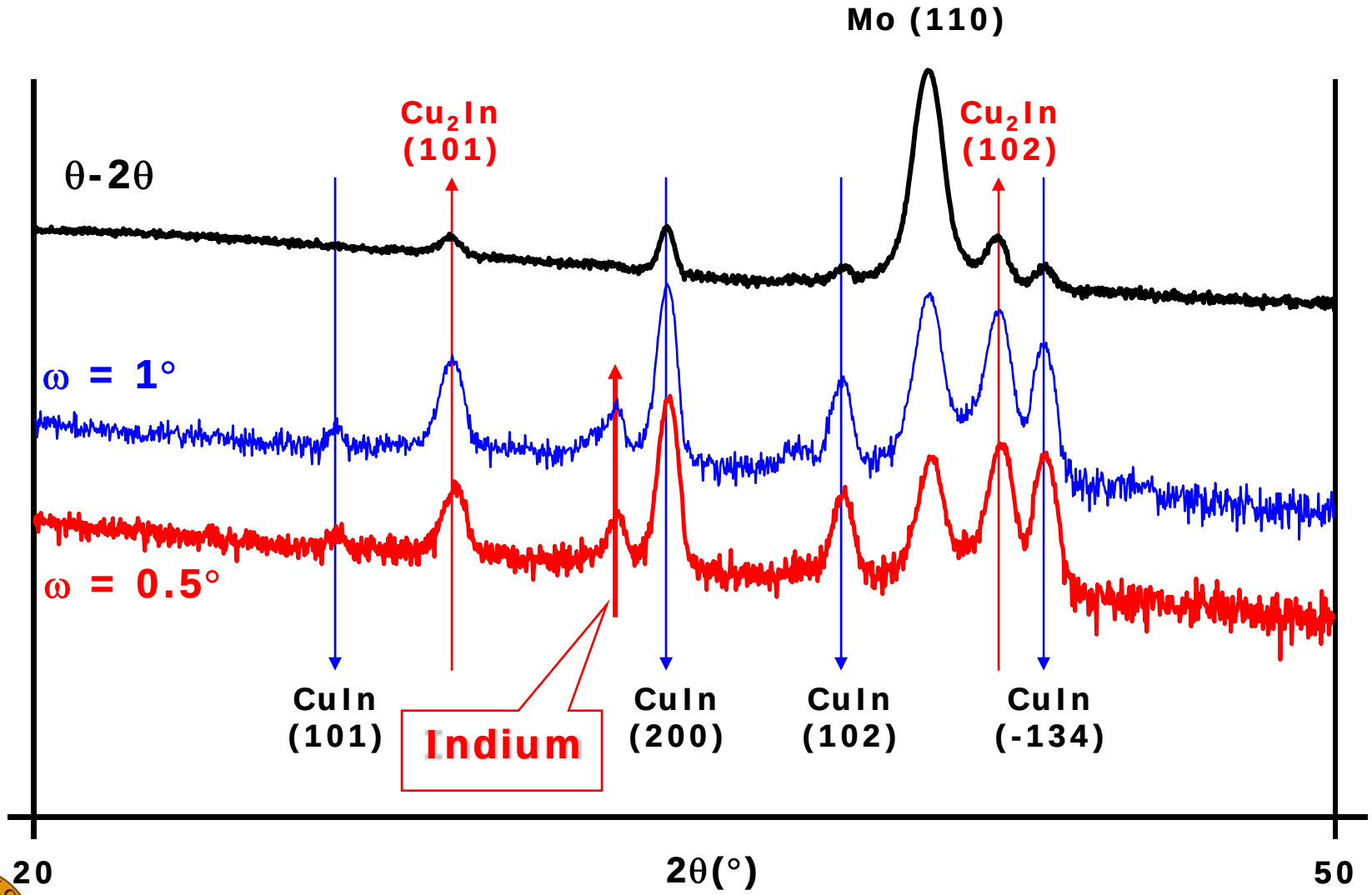
	Matrix	Island
Cu (at.%)	59.4 (±1.2)	36.0 (±1.0)
In (at.%)	40.6 (±1.2)	64.0 (±1.0)

▶**Island : In-rich or nearly pure indium phase**

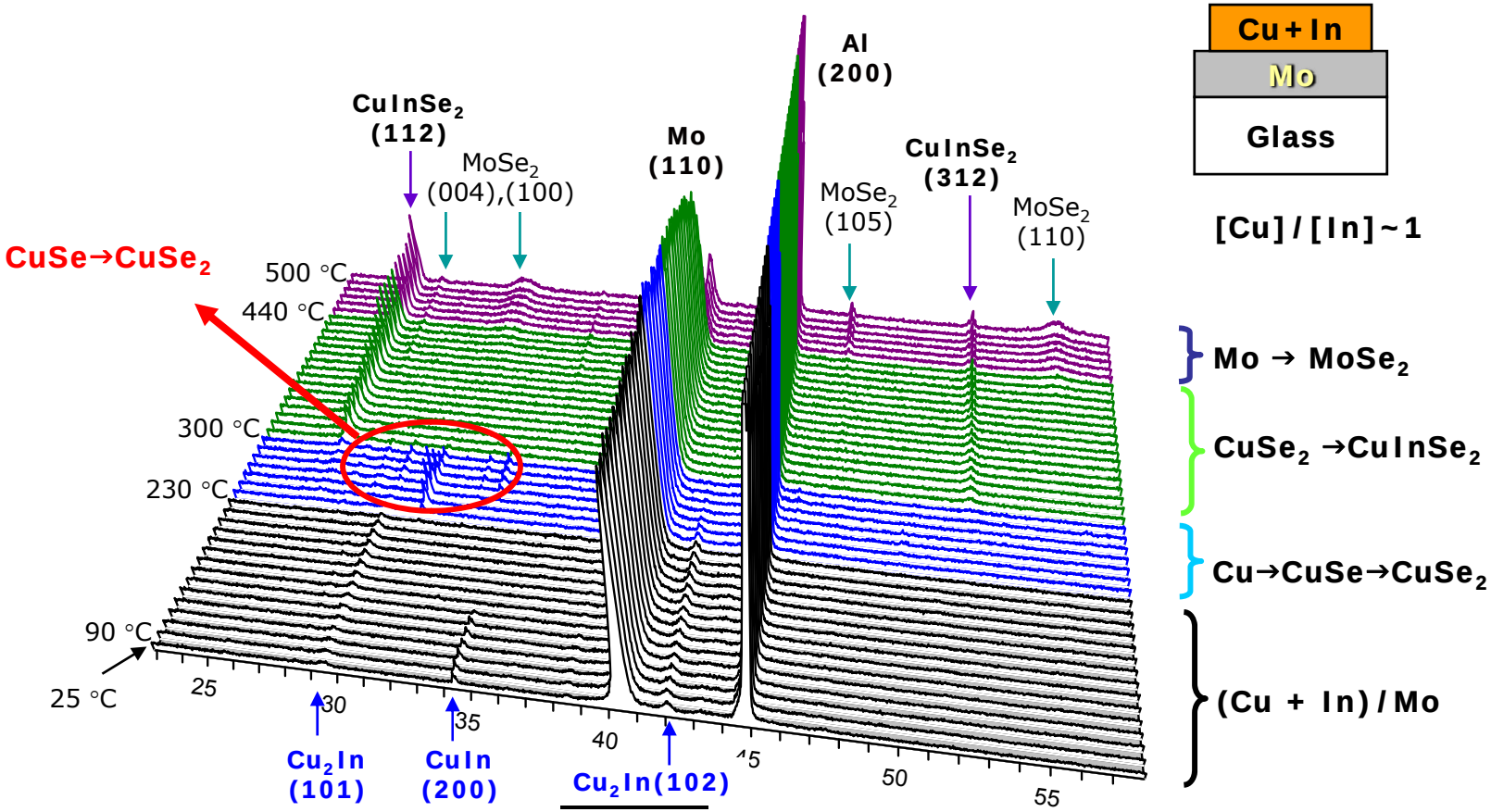


1 μm

XRD & GI-XRD for Precursor

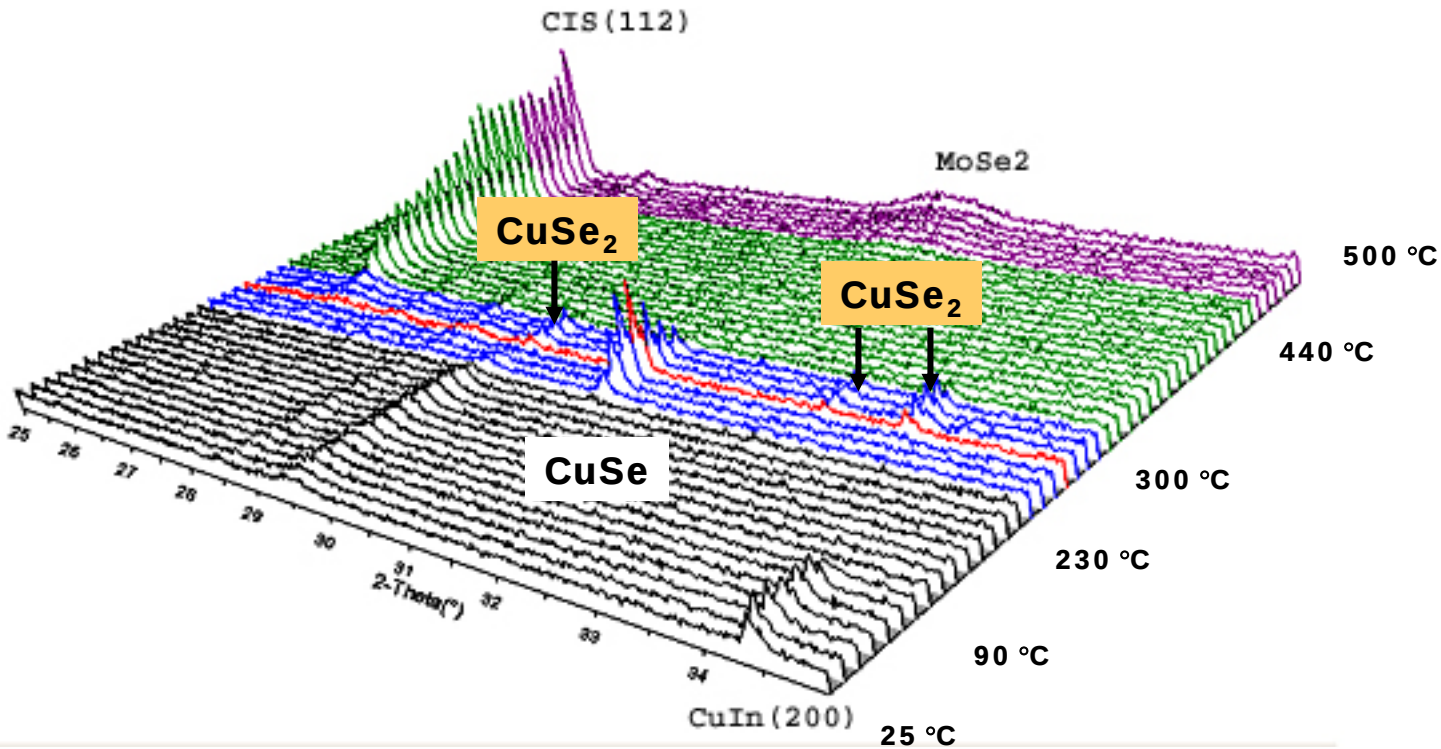


(Cu+In)/Mo Selenization



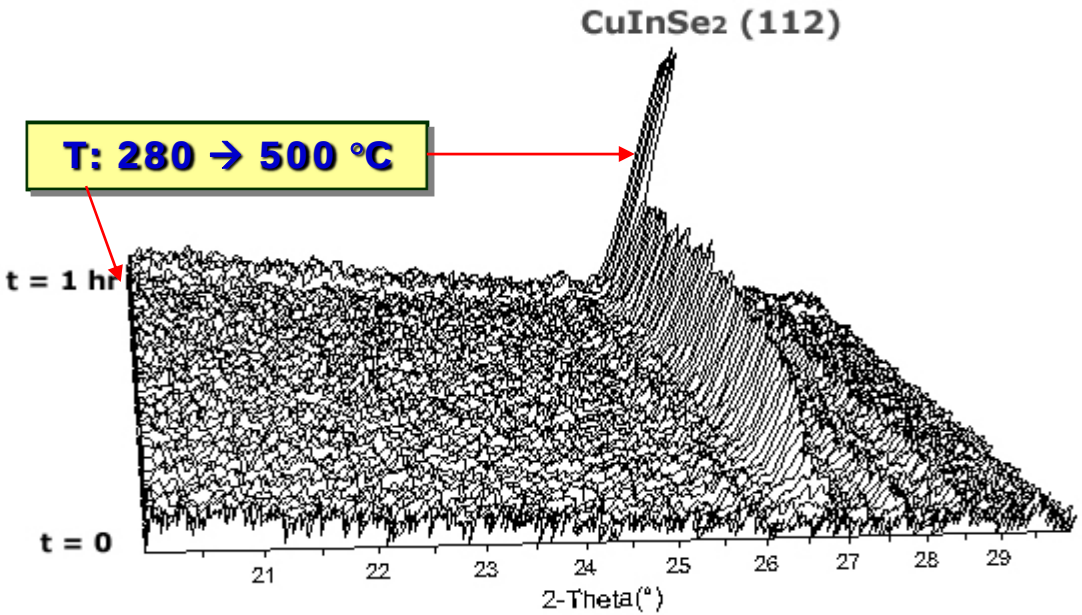
(Cu+In)/Mo Selenization

Cu/In → CuSe → $CuSe_2$ → $CuInSe_2$



Isothermal Selenization

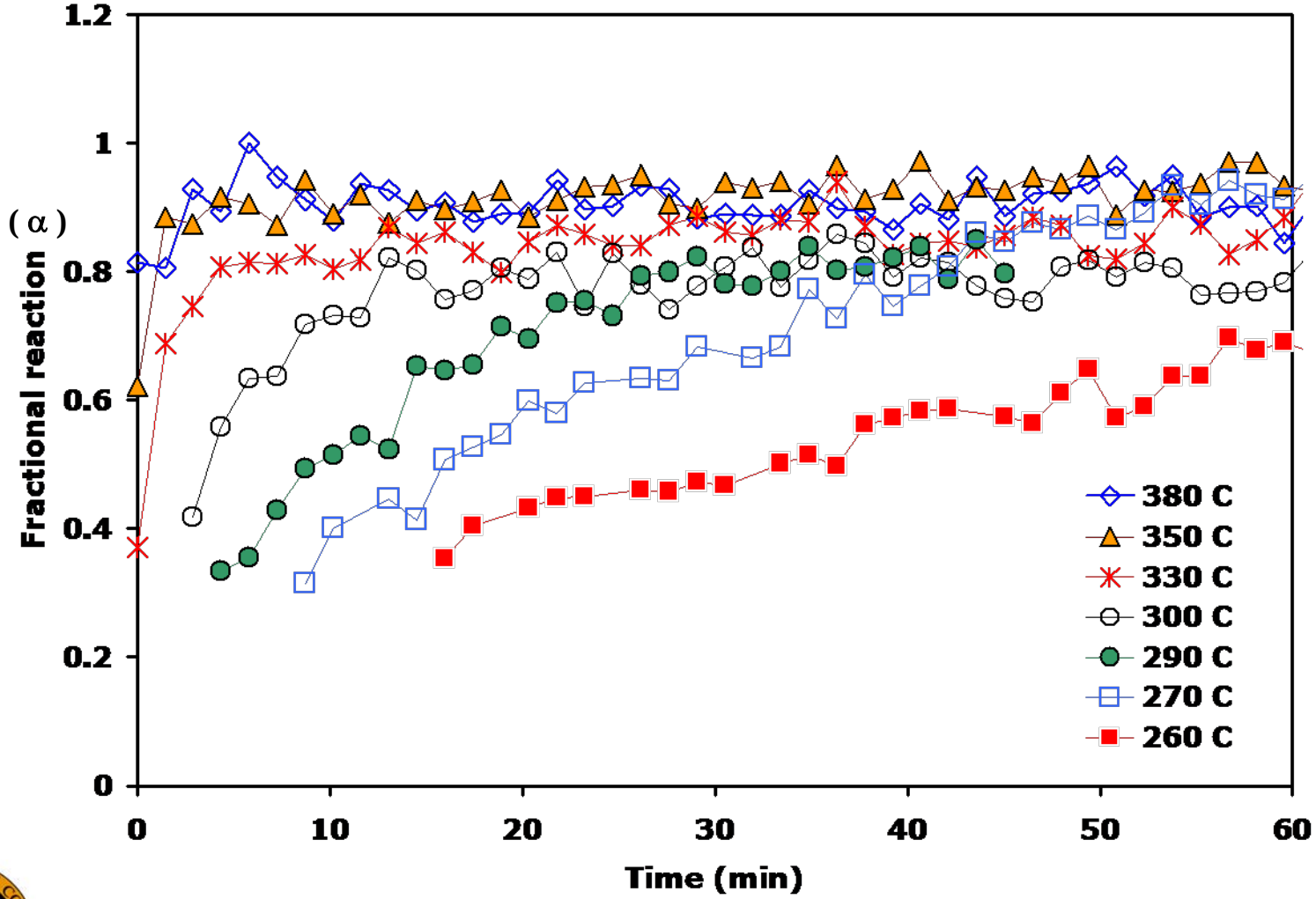
Temperature = 280 °C



■ Assumption for kinetic analysis

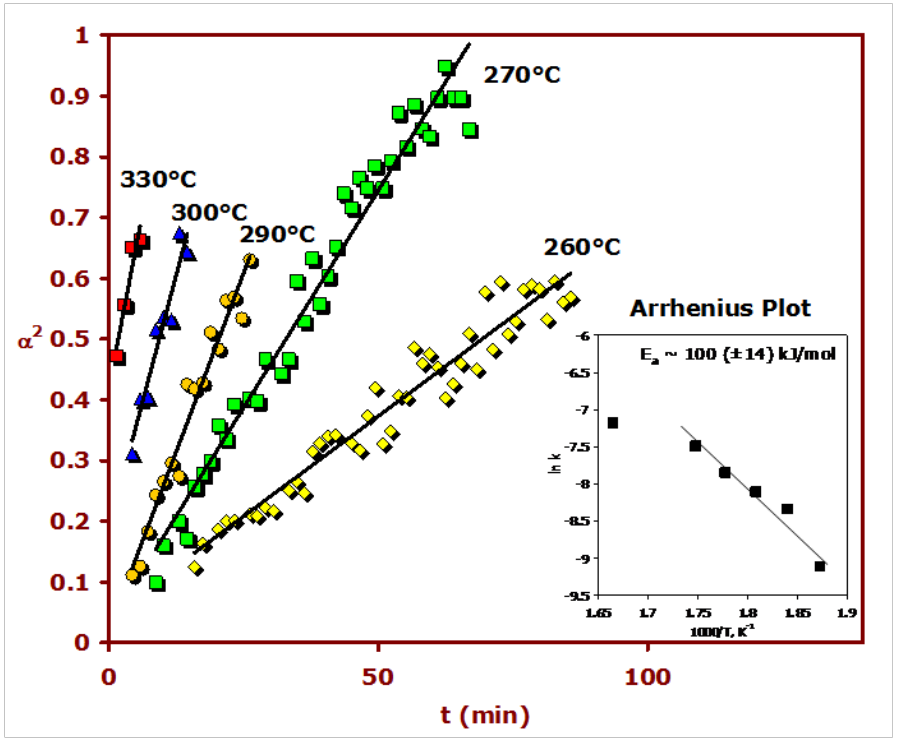
➔ **Largest peak area = 100 % reaction**
➔ **Fractional reaction = normalized peak area**

Fractional Reaction



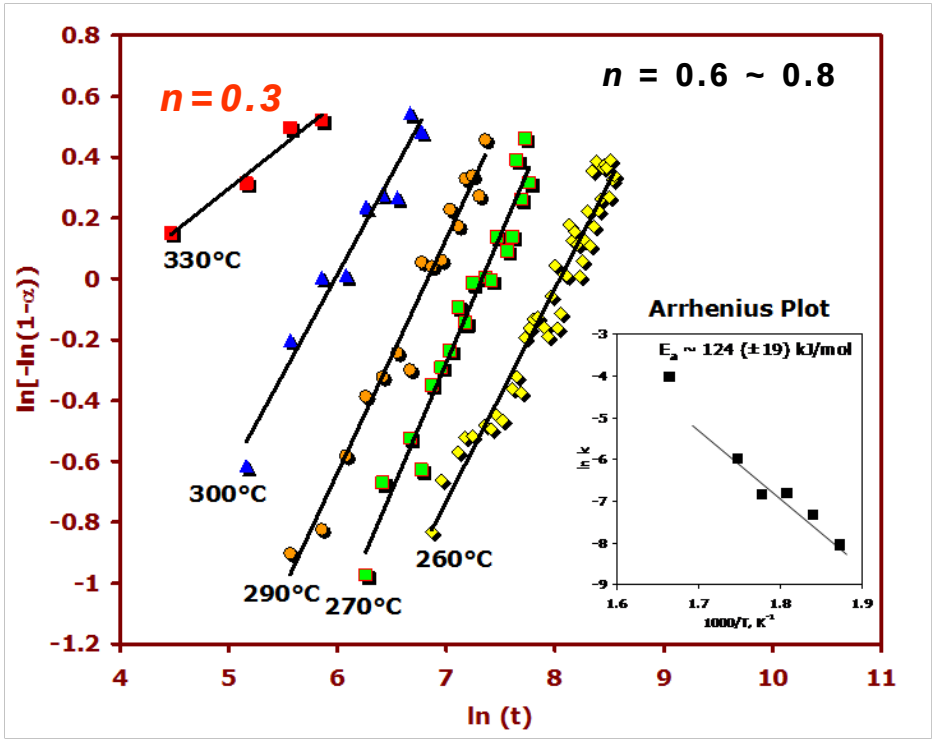
Kinetic Analysis

Parabolic model



$\alpha^2 \sim k \cdot t$

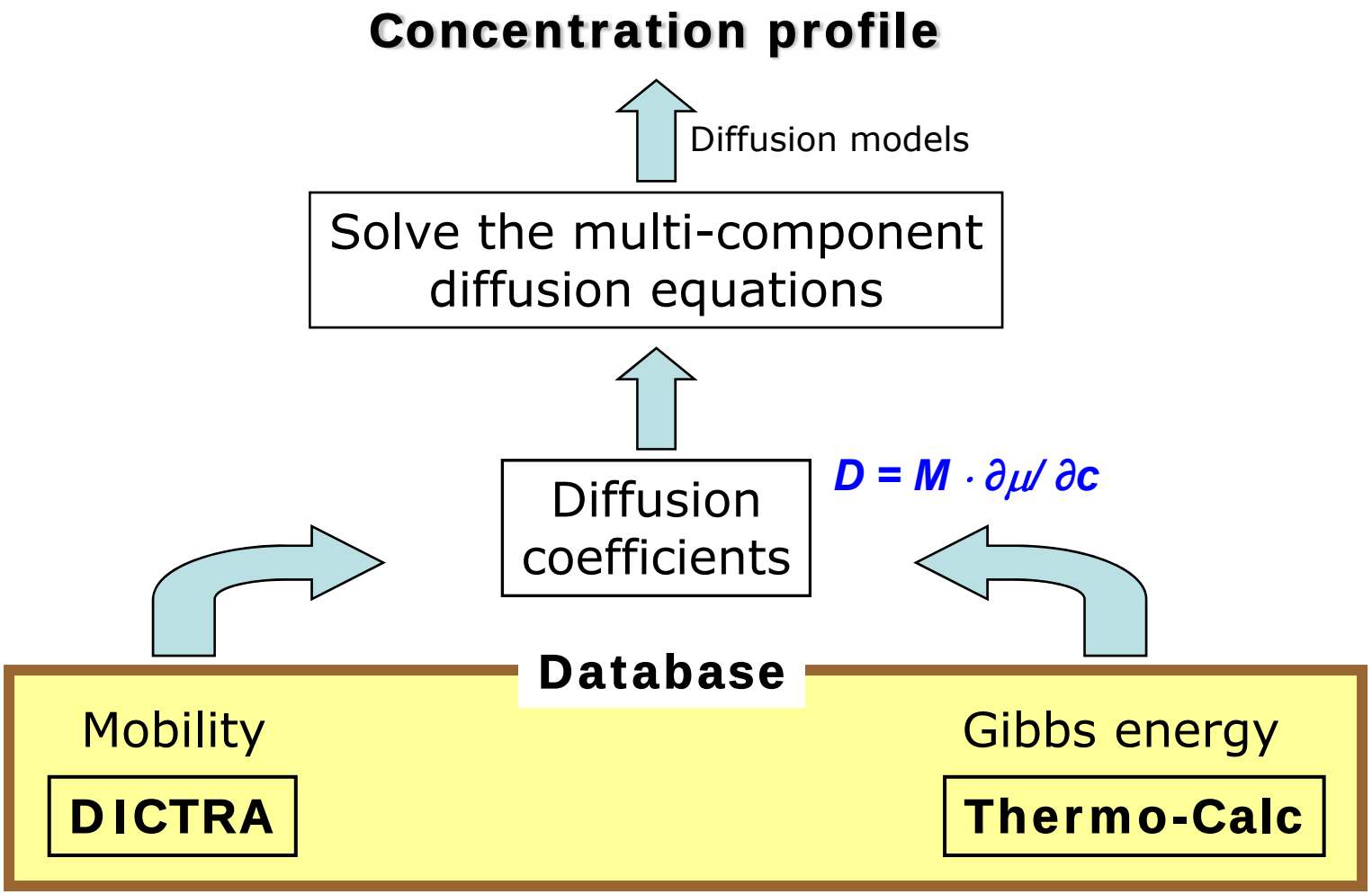
Avrami model



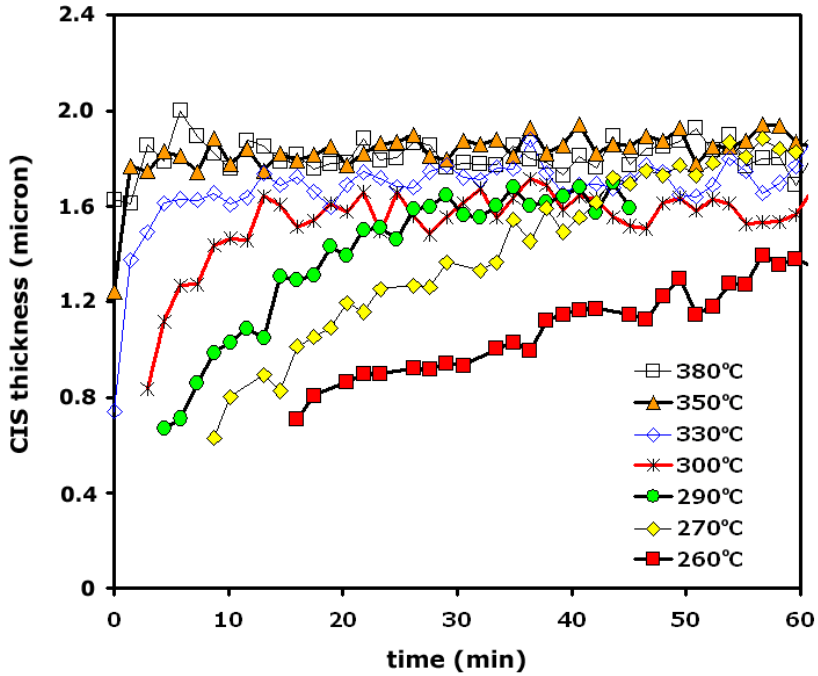
$\ln[-\ln(1-\alpha)] = n\ln(t) + n\ln k$

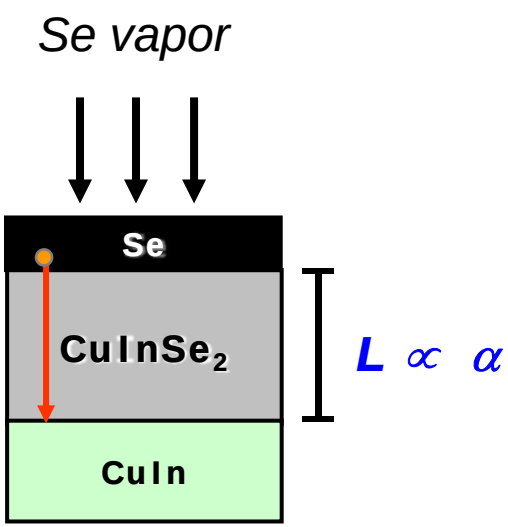
➔ *Analysis suggests one-dimensional diffusion controlled reaction*

DICTRA Modeling



DICTRA Optimization



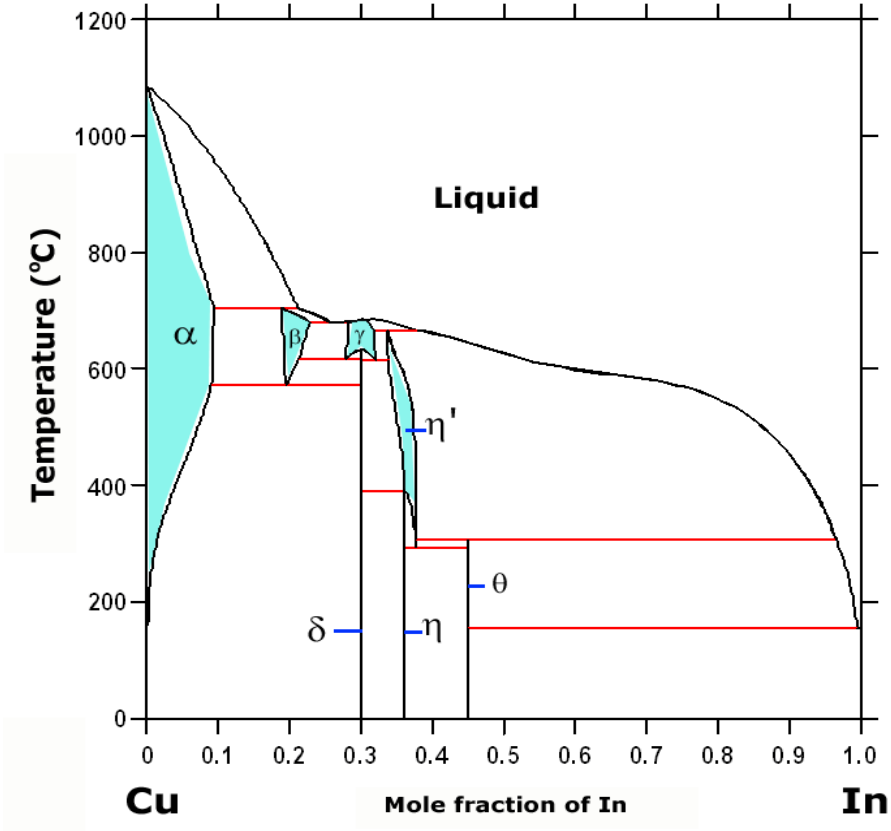


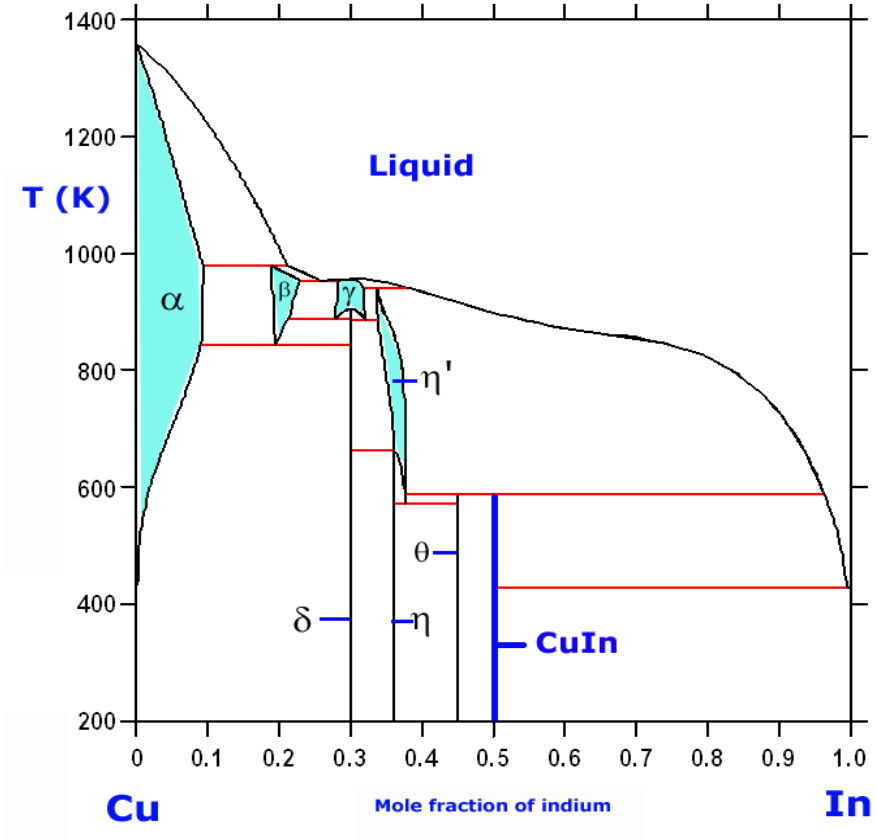
Assumption:

- ➔ Driving force: Gradient of Se chemical potential
- ➔ Control step: Diffusion of Se thru CIS layer
- ➔ Simplified pseudo-binary reaction: ***CuIn + 2Se → $CuInSe_2$***

Instead of: $mCu_2In + nCuIn + mIn + (4m+2n)Se \rightarrow (2m+n)CuInSe_2$

Cu-In Thermodynamic Database





H. S. Liu, et al., J. Phase Equilib. 23 (2002) 409

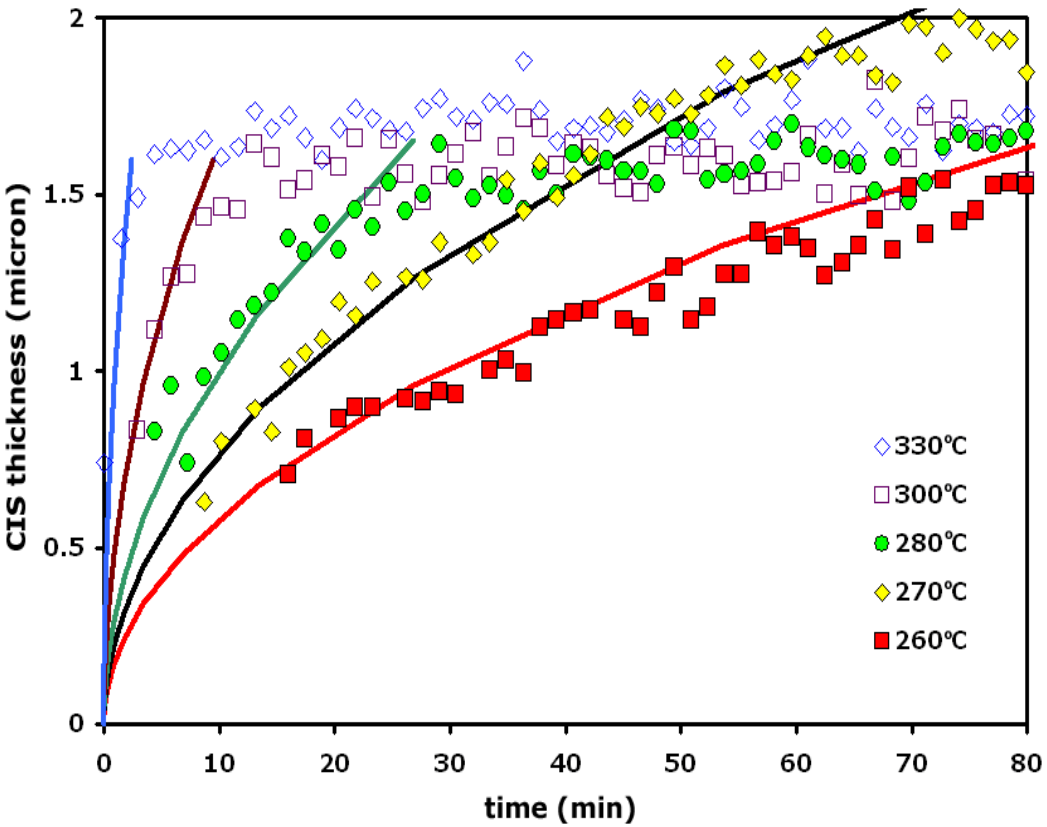
DICTRA Optimization Results

Mobility parameter in DICTRA

$$MQ = -Q_B + RT\ln(M_B^0)$$

Q_B: activation enthalpy
(= 136,725 J/mol)

M_B^0: frequency factor
(= 0.01406)



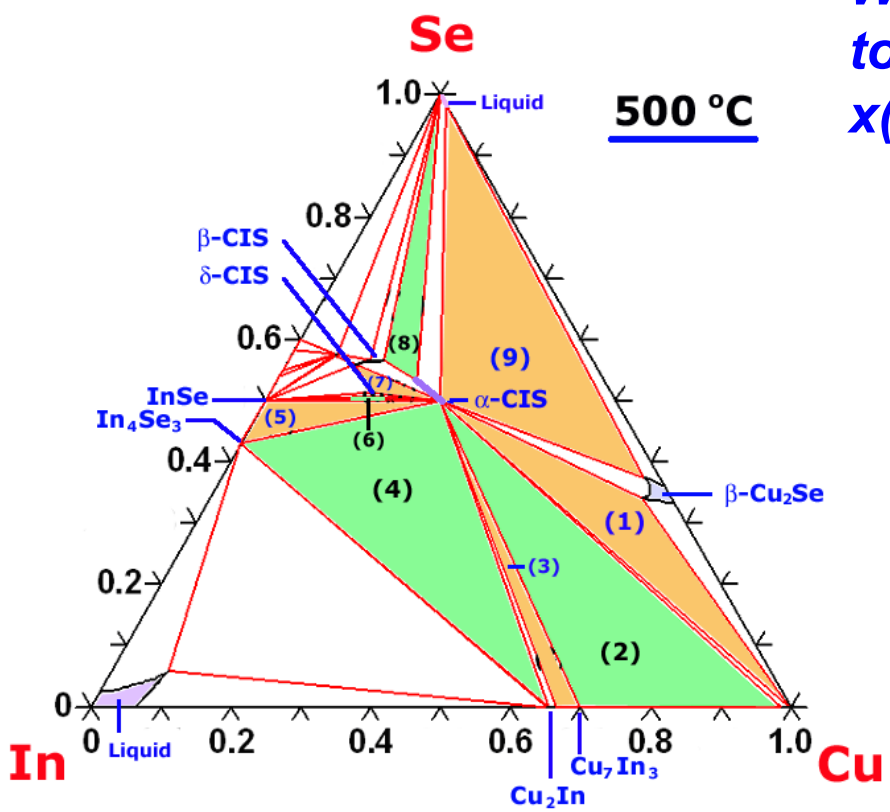
Summary

- *In-situ* HT-XRD was successfully employed to investigate the reaction pathways and kinetics of binary and ternary diffusion couples.
- Kinetic data was used to get Se mobility database using DICTRA optimization.
- Systematic efforts on Cu-In-Ga-Se diffusion database establishment will be necessary to optimize high quality CIGS formation process.

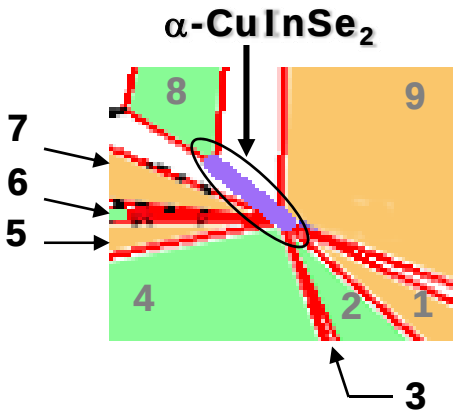
Appendix

Ternary Cu-In-Se Phase Diagram

Isothermal section at 500 °C

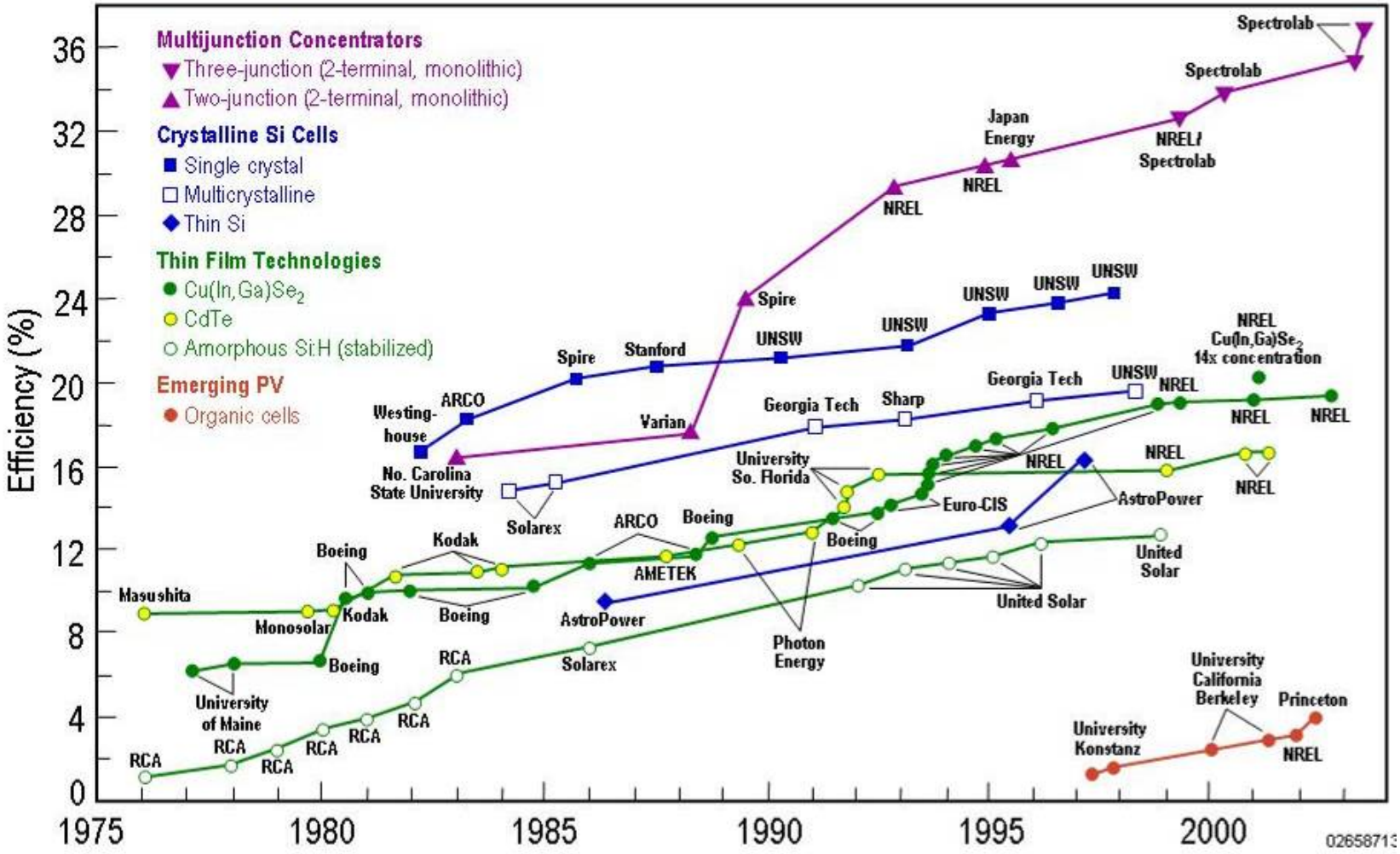


Wide composition tolerance !!
x(Cu) = 21~25 at.%

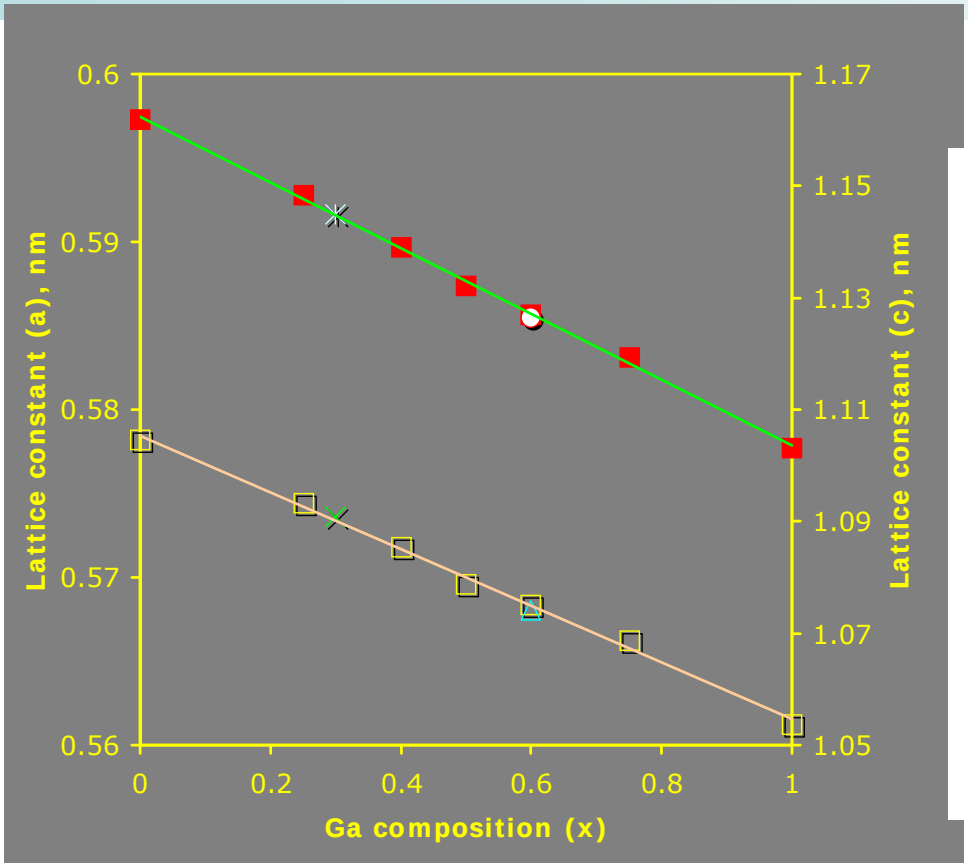


Region	Equilibrium phases
1	α-$CISe_2$ + α-Cu + β-Cu_2Se
2	α-$CISe_2$ + α-Cu + Cu_7In_3
3	α-$CISe_2$ + Cu2In + Cu_7In_3
4	α-$CISe_2$ + Cu2In + In_4Se_3
5	α-$CISe_2$ + InSe + In_4Se_3
6	α-$CISe_2$ + InSe + δ-$CuInSe_2$
7	α-$CISe_2$ + β-$CuIn_3Se_5$ + δ-$CuInSe_2$
8	α-$CISe_2$ + β-$CuIn_3Se_5$ + Liquid
9	α-$CISe_2$ + β-Cu_2Se + Liquid

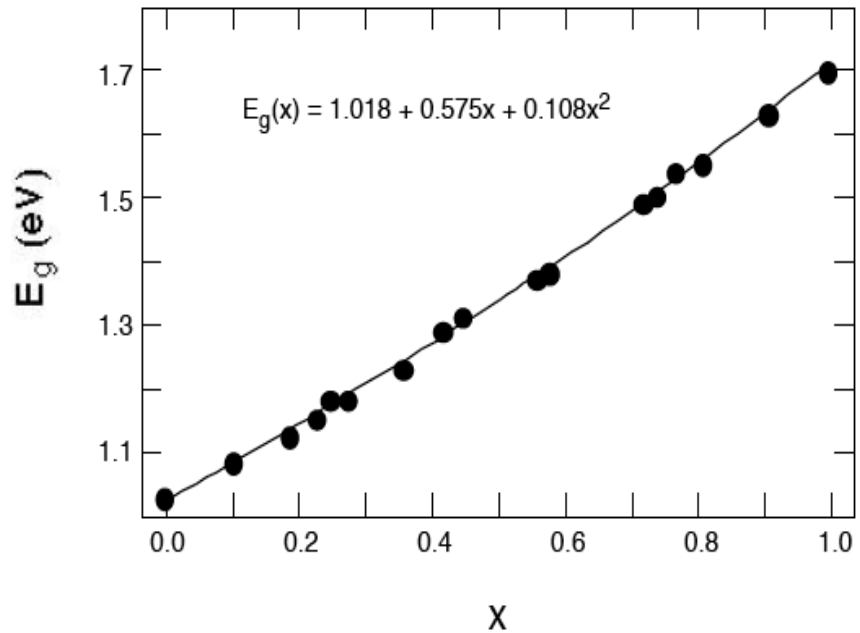
Best Efficiency of Solar Cells



Ga addition ?



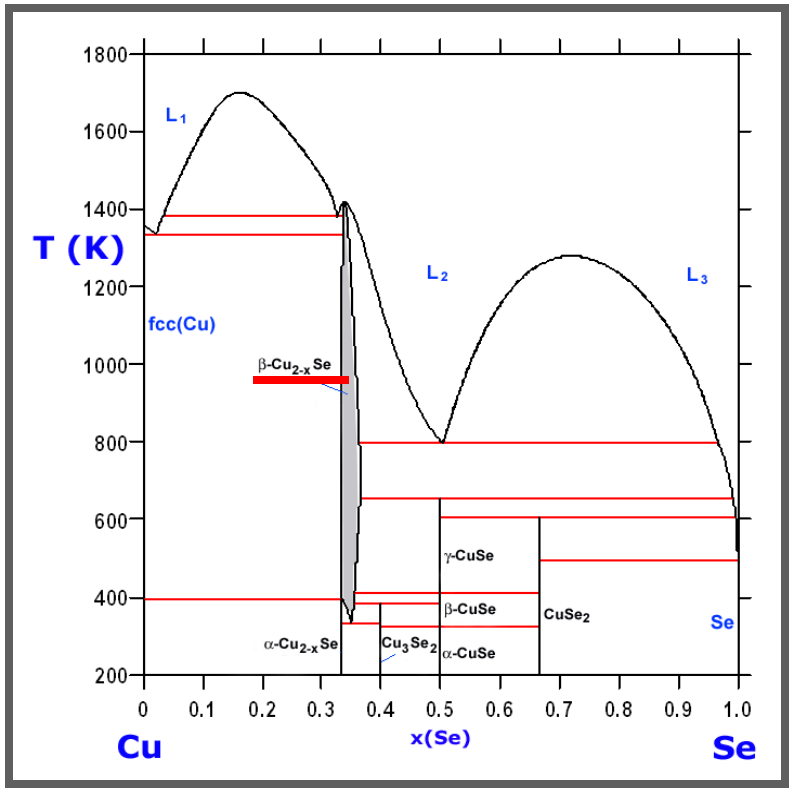
Bandgap energy



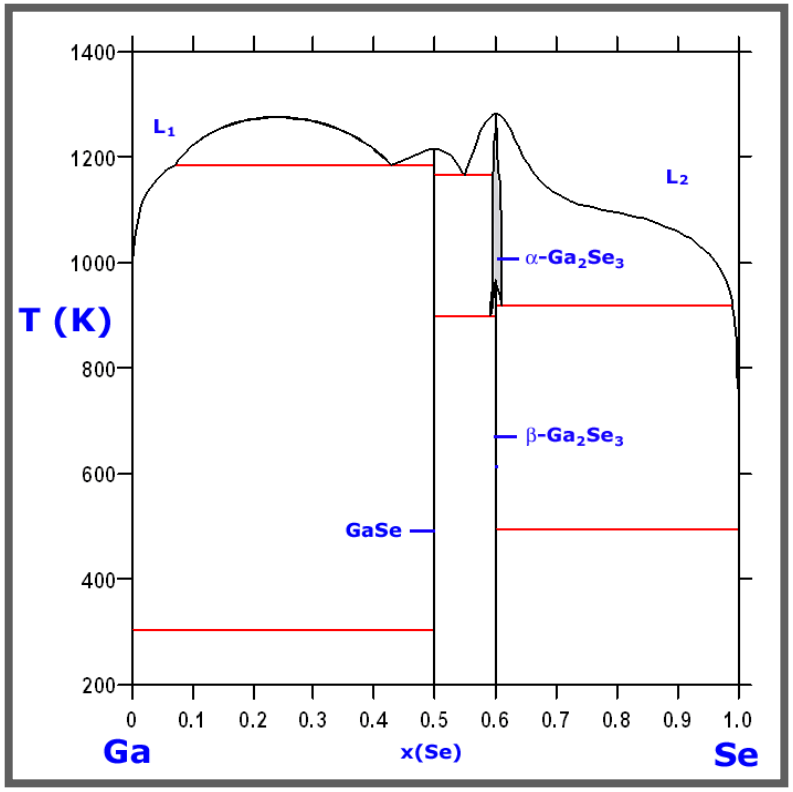
	Lattice constants		Bandgap energay Eg (eV)	Absorption coefficient α (cm^{-1})
	a (nm)	b (nm)		
$CuInSe_2$	0.5784	1.1614	1.04	~ 1×10^5
$CuGaSe_2$	0.5596	1.1002	1.68	> 3×10^4

Binary Phase Diagram

Cu-Se



Ga-Se



Diffusivity and Mobility

Diffusion coefficients are obtained as a product of a thermodynamic ($\partial\mu/\partial c$) and a kinetic (M) factor.

$$D = M \cdot \partial\mu/\partial c$$

$$M = M_b + \exp(M_q/RT)$$

Formation of CIS by selenization of Cu+In precursor

- Driving force: Gradient of chemical potential of Se
- Control step: Diffusion of Se thru CIS layer
- Key data:
  - Chemical potential of Se in different phases
  - Mobility of Se in CIS phase

- DICTRA optimization results:

  $M_b=0$

  $M_q=-168000$ J/mol

  M_q remains constant for the entire range of experimental temperatures.