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

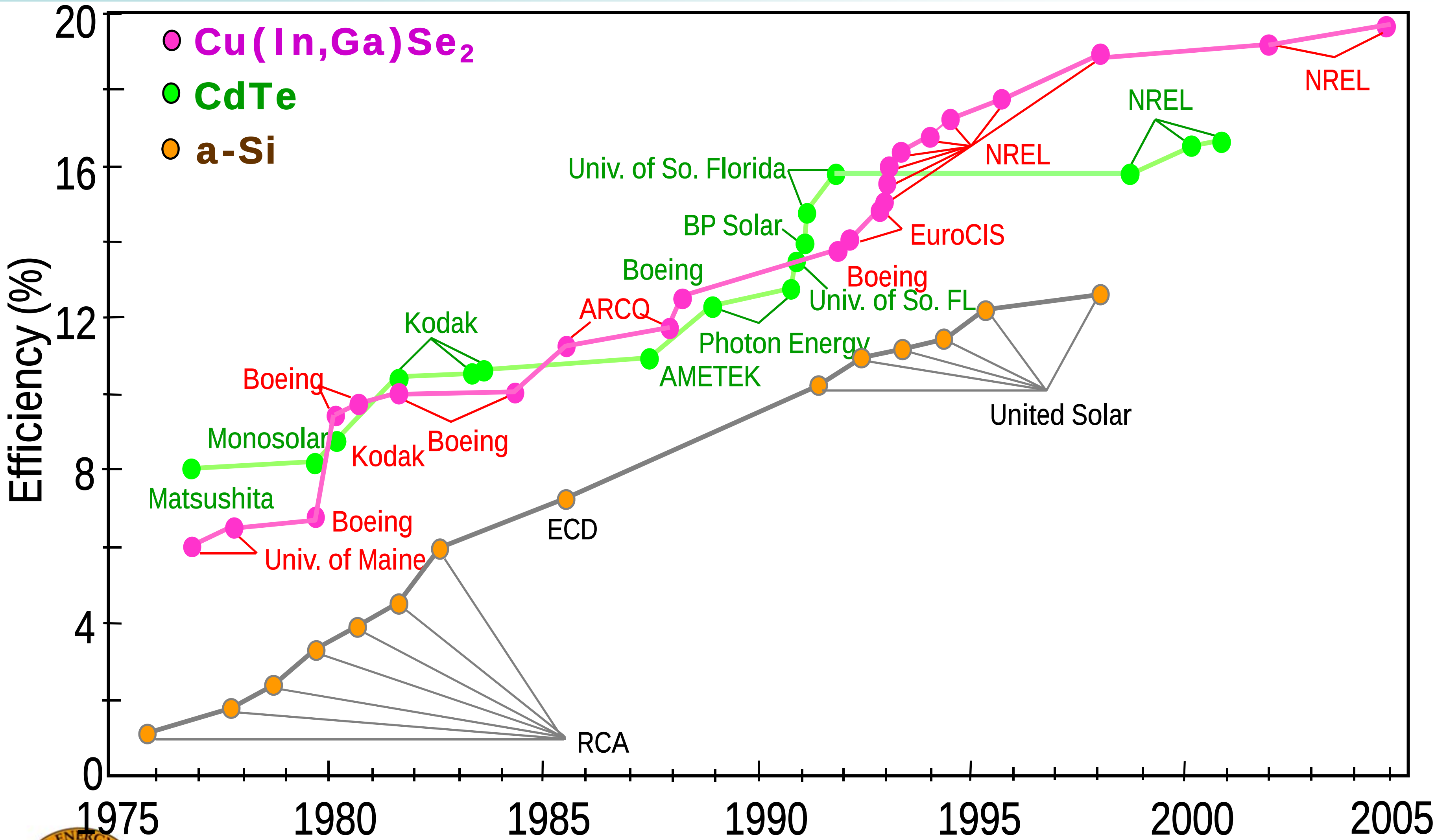
Thin Film CIGS Solar Cells

Building-integrated CIGS, 85kW Shell Solar

GLOBAL SOLAR
Systems That Deliver

Flexible, lightweight Cu(InGa)Se_2 - Global Solar

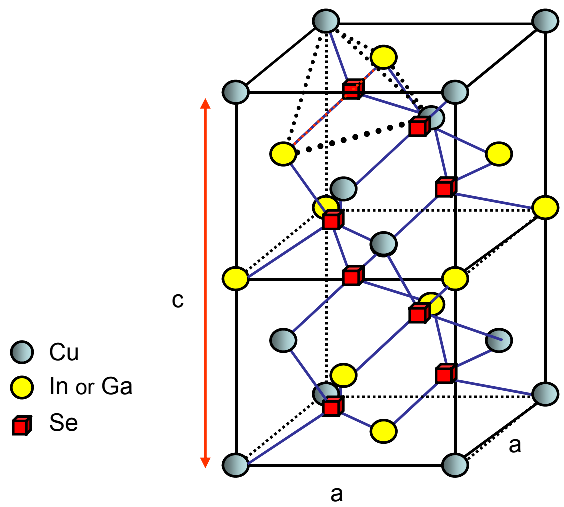
Best Efficiency of Thin Film Cells



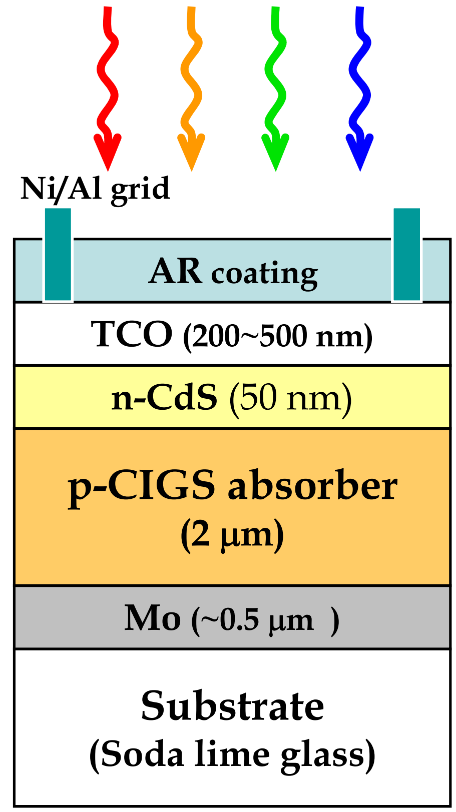
$Cu(In,Ga)Se_2$ Solar Cells

■ 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



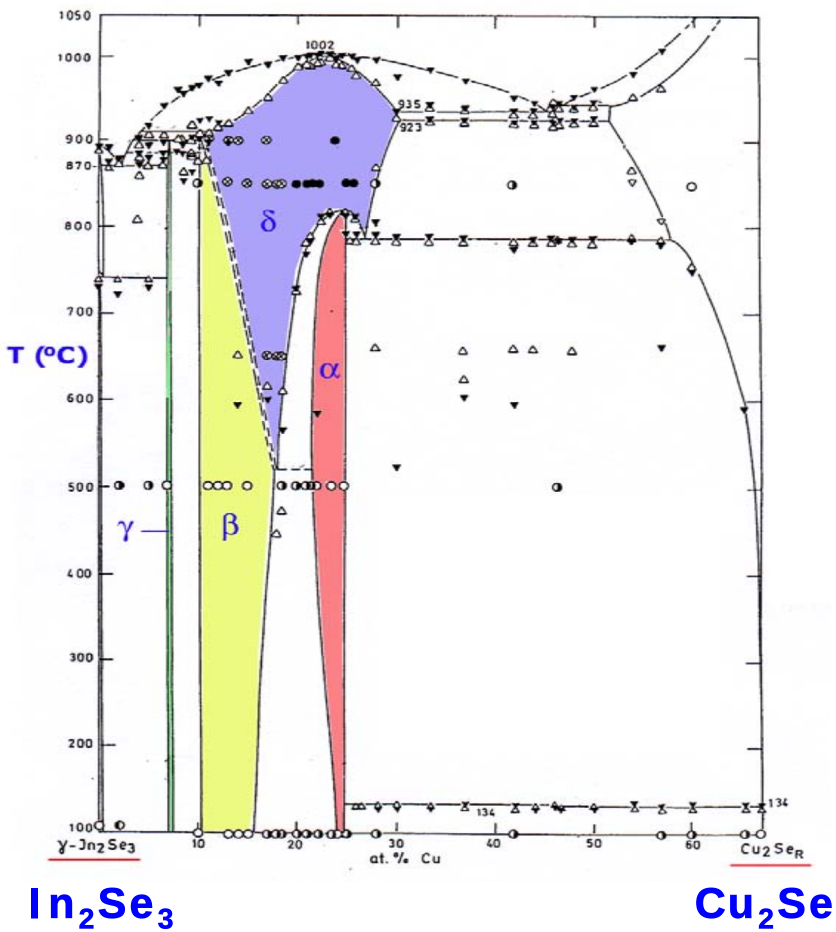
Chalcopyrite CIGS structure



Typical device structure

Cu-In-Se Phase Equilibrium

Cu_2Se-In_2Se_3 pseudo-binary



Wide composition tolerance of chalcopyrite α-CuInSe$_2$

x(Cu) = 21~25 at.%

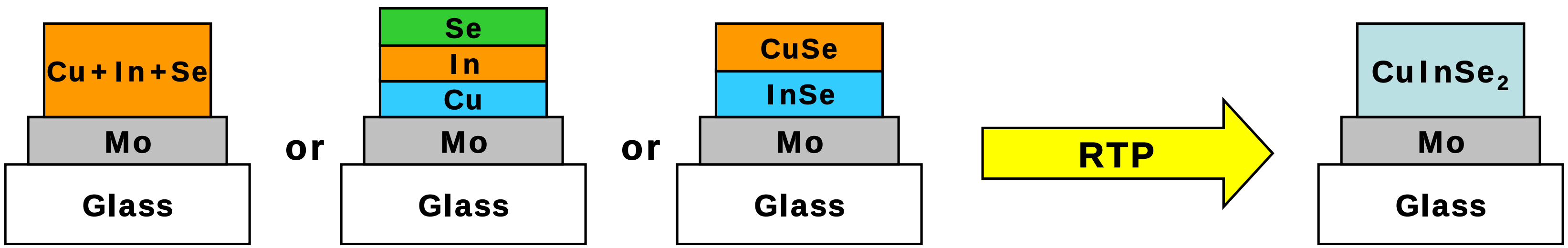
δ : *CuInSe$_2$ – sphalerite*
β : *CuIn$_3$Se$_5$ – ODC*
γ : *CuIn$_5$Se$_8$ – ODC*

T. Gödecke et al., Z. Metallkd (2000)

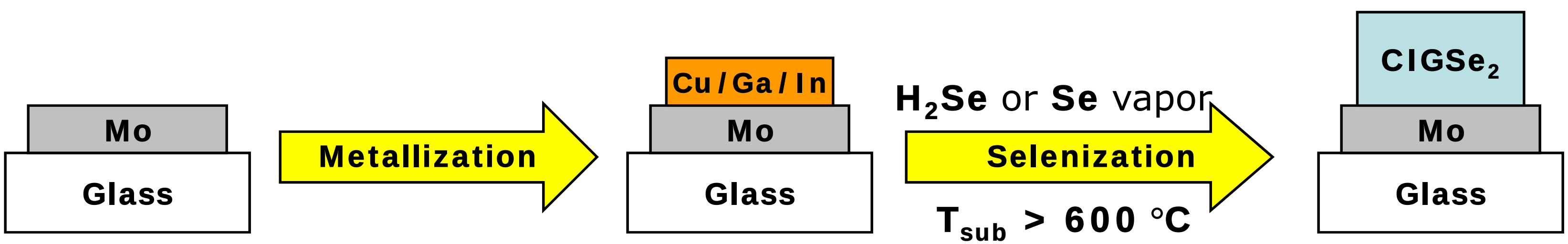
Common Deposition Techniques

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

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

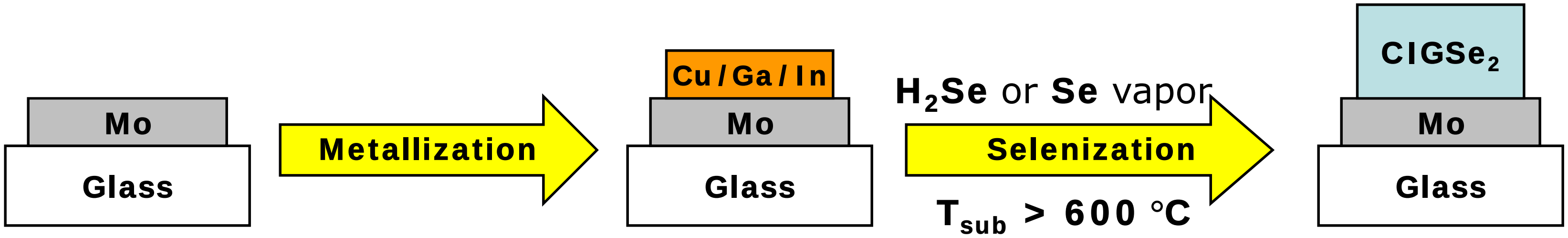


- Selenization of metallic precursors: ***"Shell Solar" 2 step method***



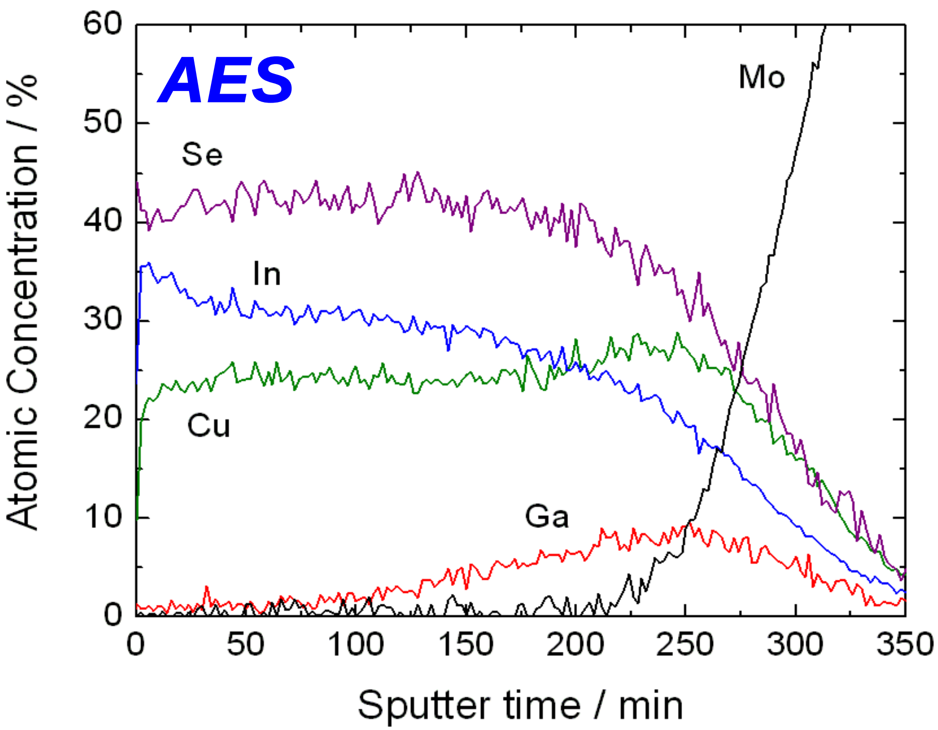
Diffusion Issues

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



Ga accumulation at back !

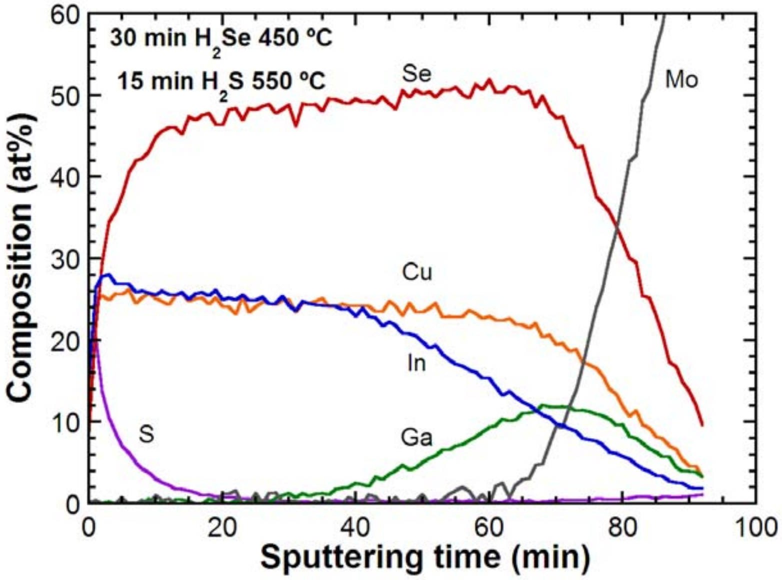
Decrease device performance !



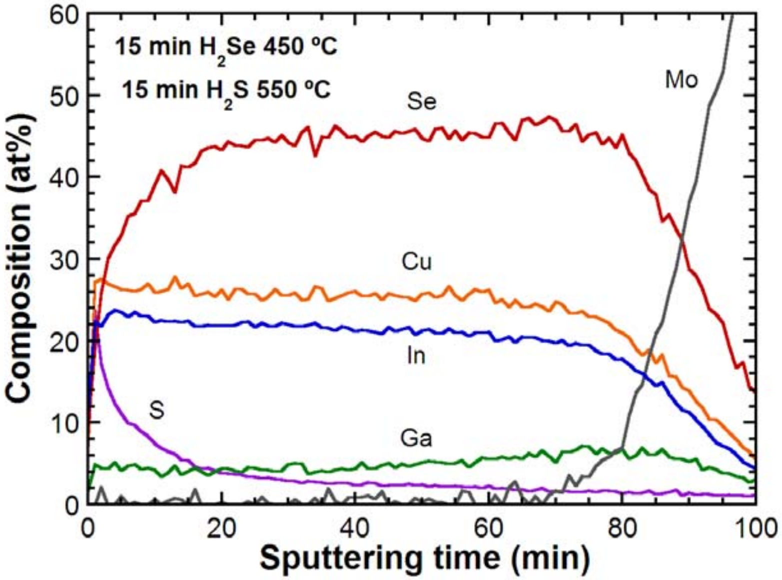
Diffusion Issues

Cu-Ga-In/Mo —— 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*



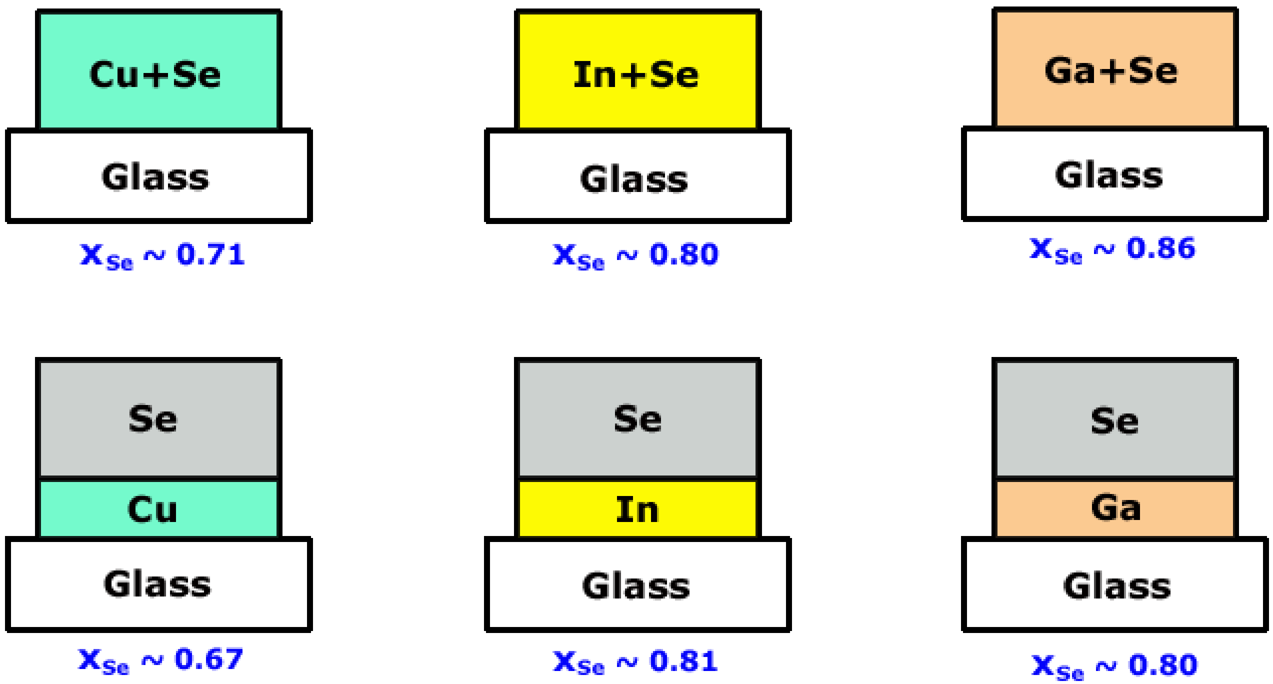
G. Hanket, W. Shafarman, R. Birkmire. , Proc. 4th World Conf. on PVEC (2006).

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

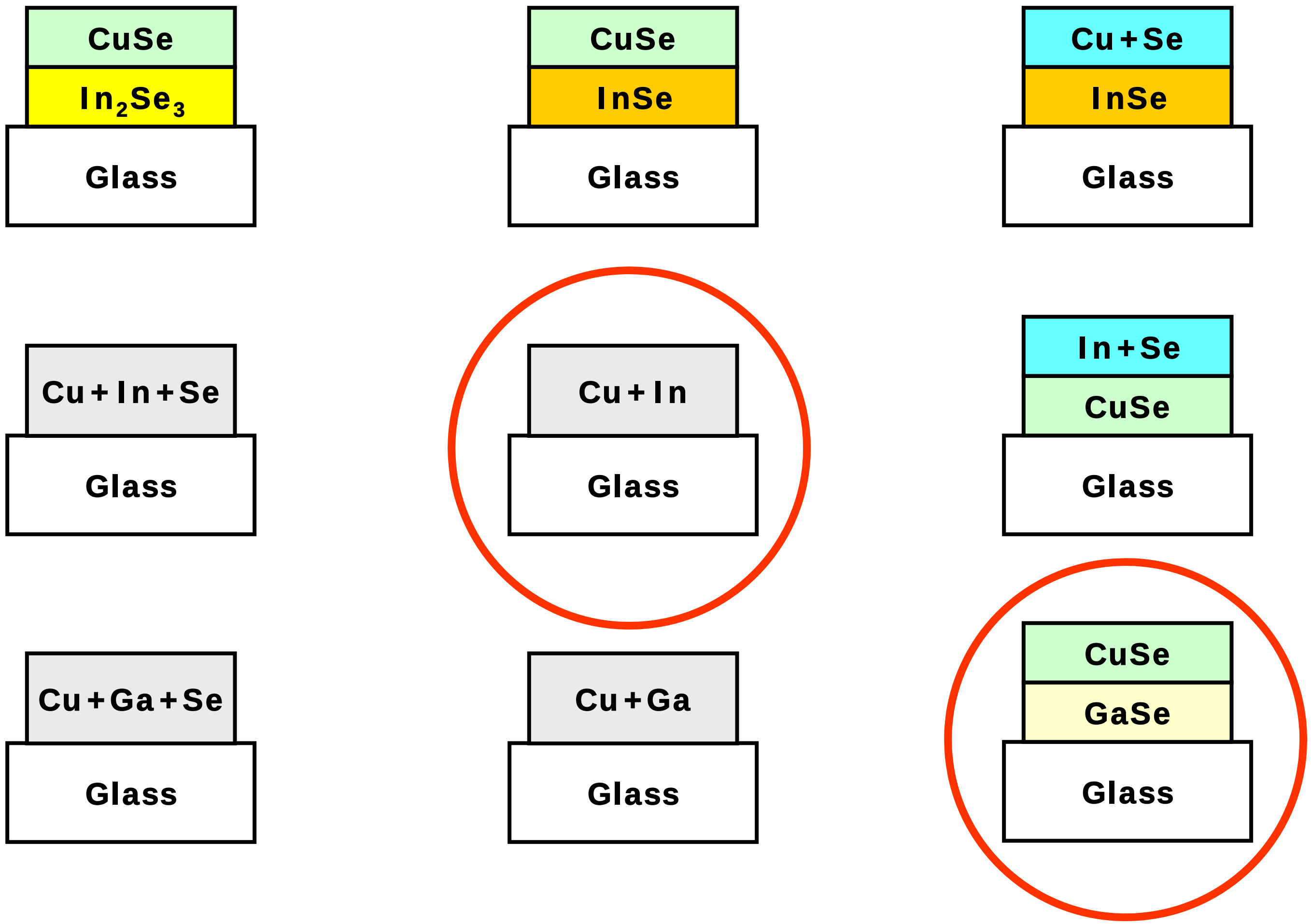
Institute of Energy Conversion
University of Delaware

NIST Diffusion Workshop
May 12, 2008

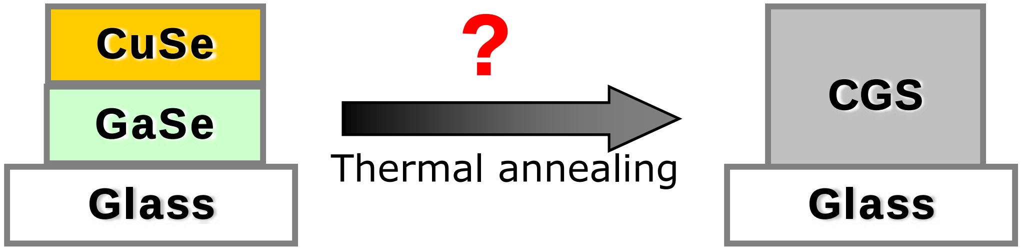
Precursor Diffusion Couples



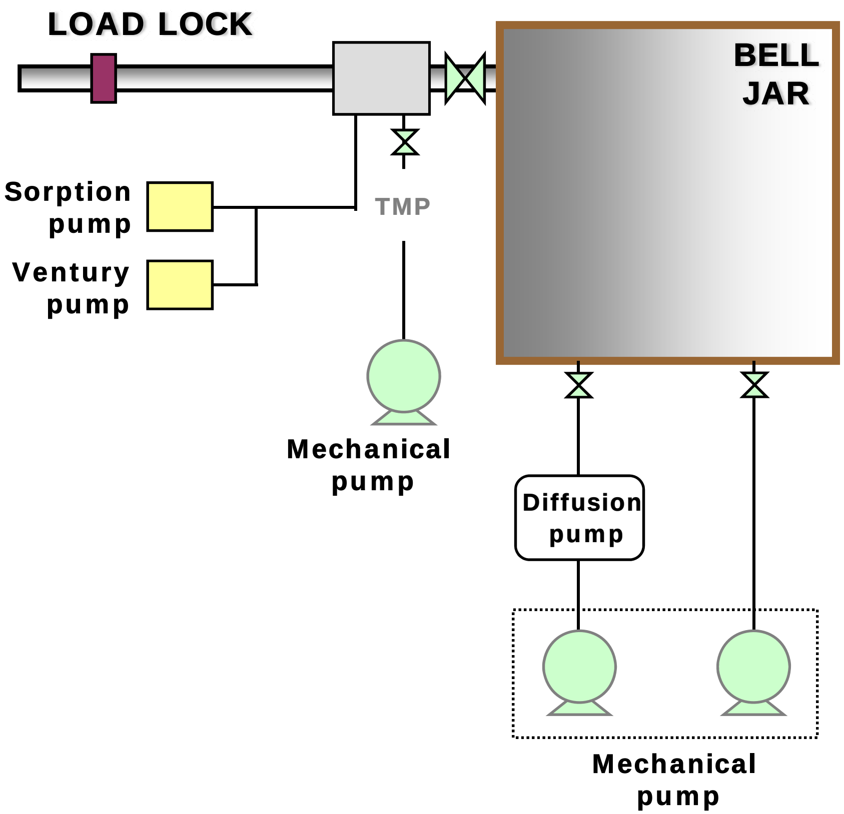
Precursor Diffusion Couples



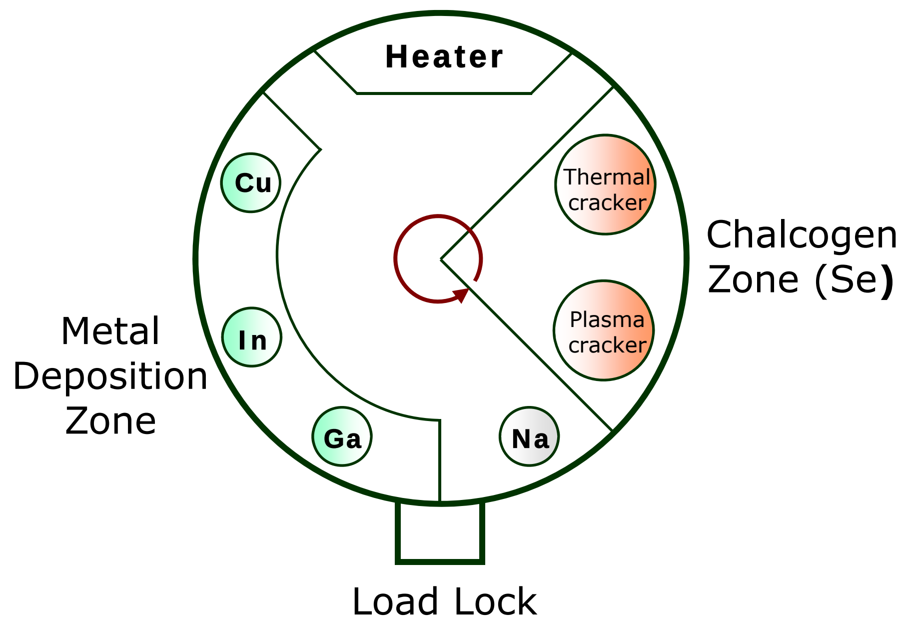
$CuGaSe_2$ formation from a bilayer GaSe/CuSe diffusion couple



Precursor Preparation by MEE System



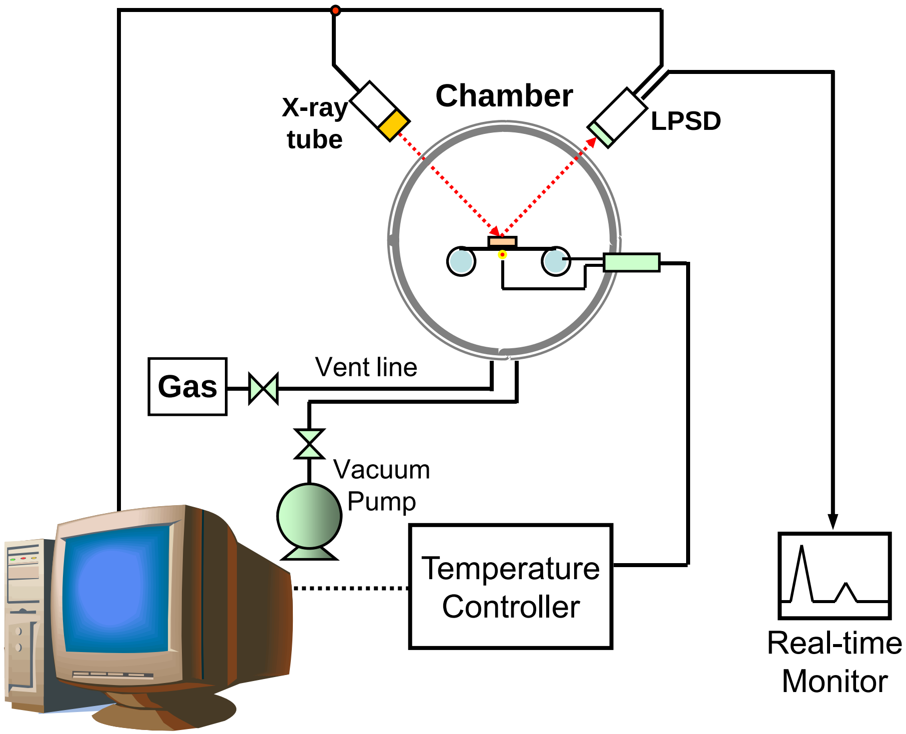
Schematic top view

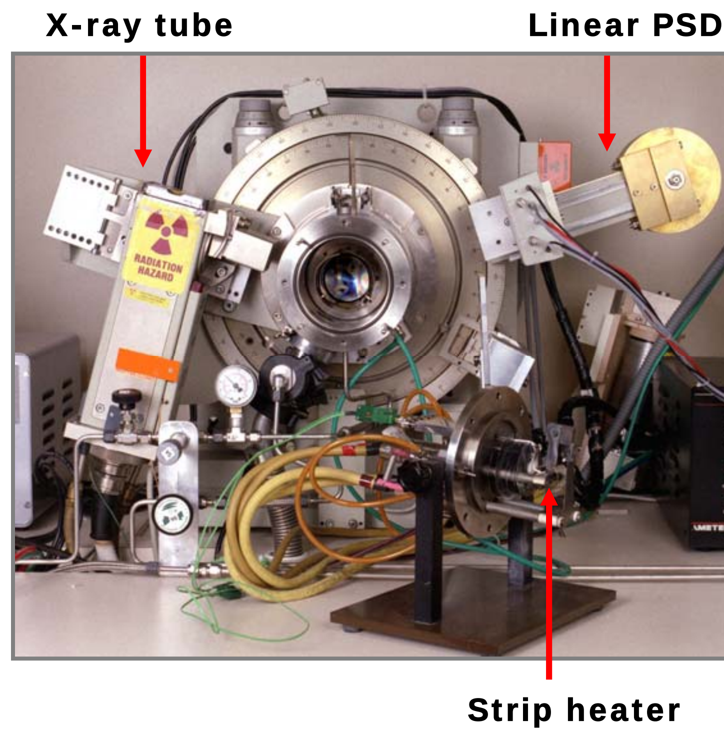


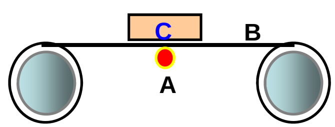
➔ Ultra high vacuum system
➔ Operating pressure : ~ 10^{-8} Torr

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

HT-XRD System



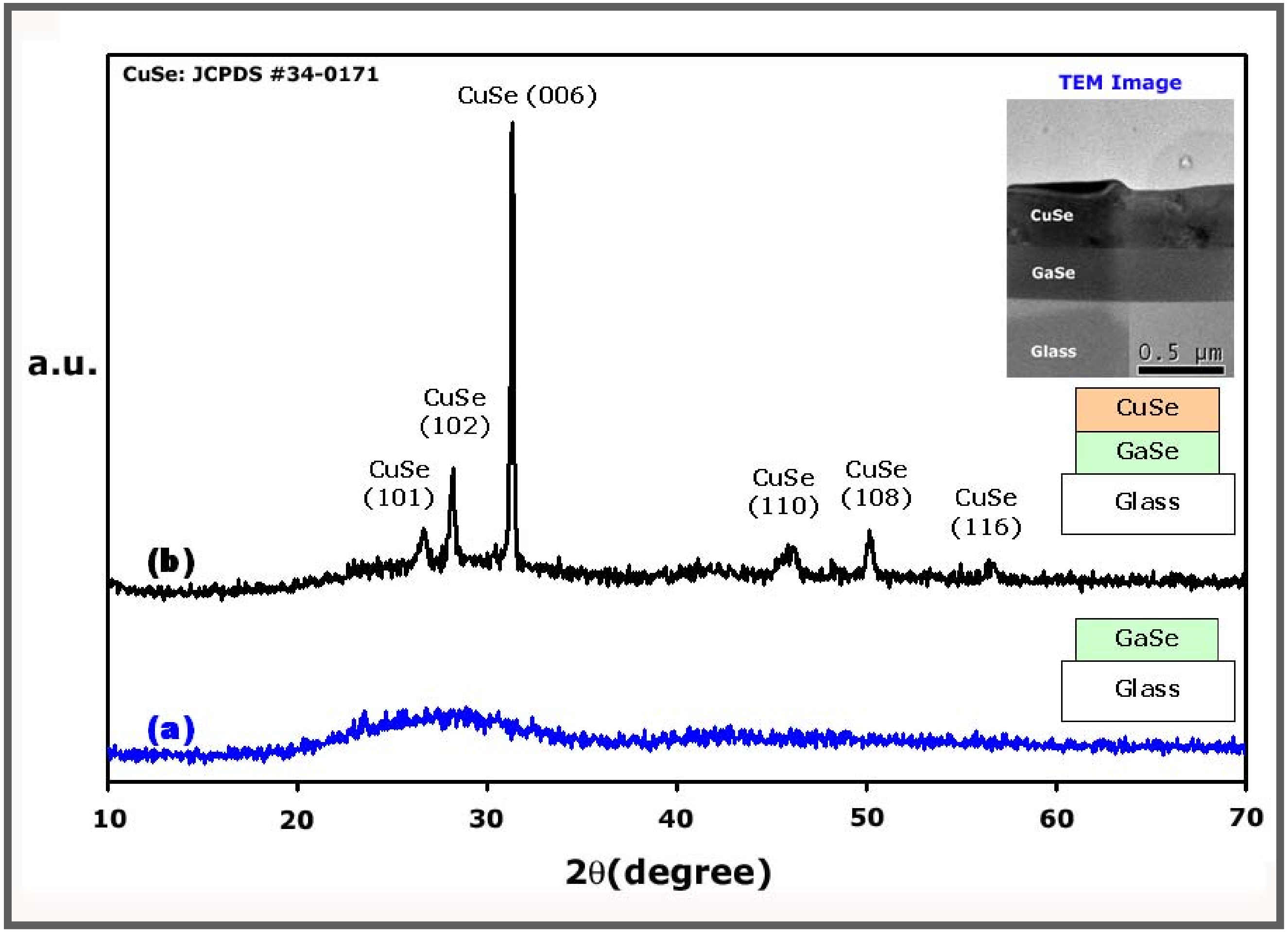




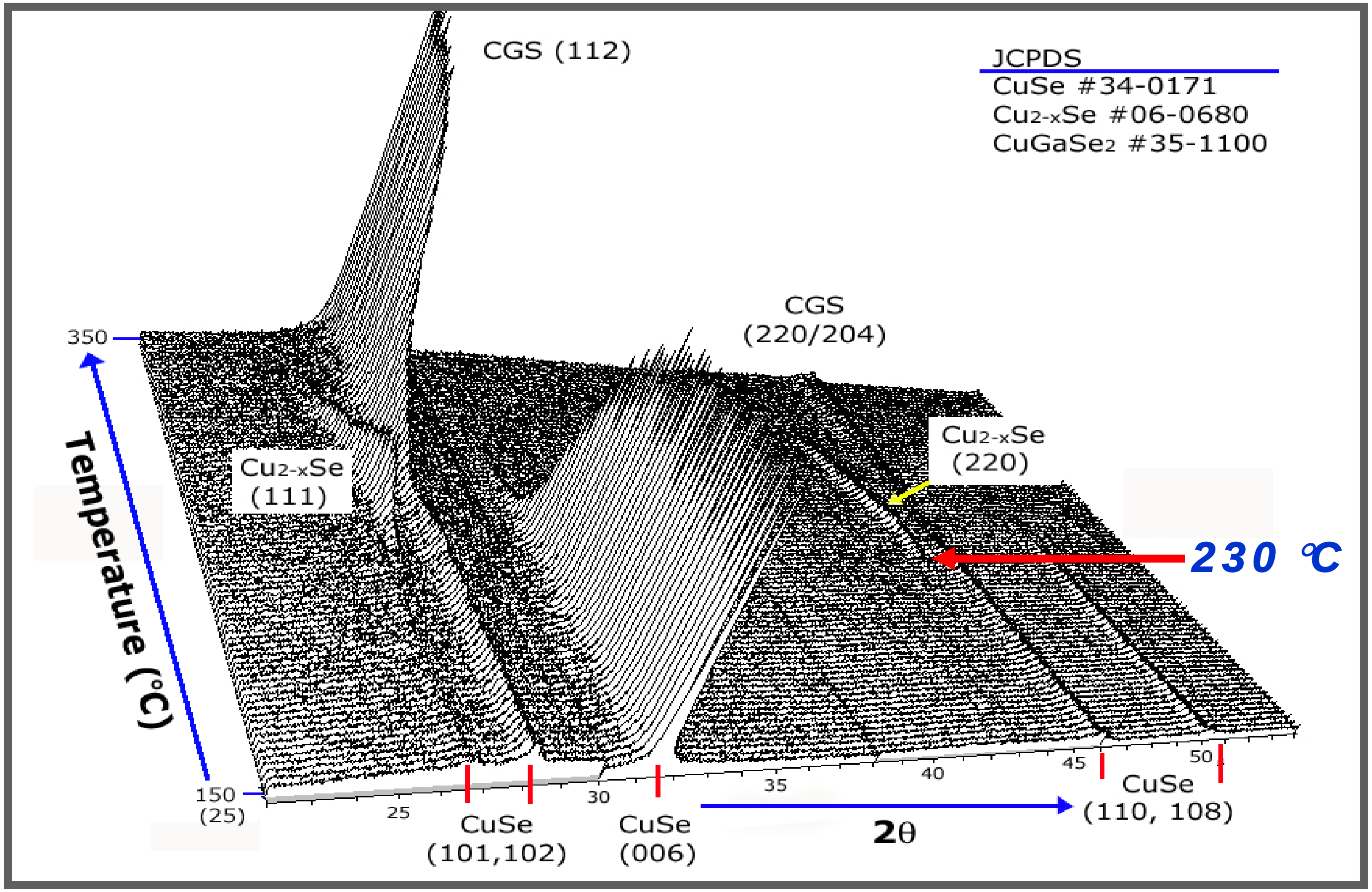
A: Spot-welded thermocouple
B: Heater strip (Pt20%Rh)
C: Sample

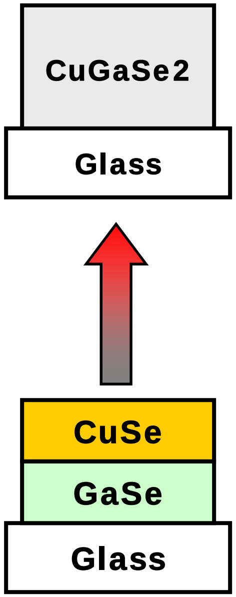
➔ ***High Temperature Materials Laboratory of Oak Ridge National Lab.***

Precursor Structure



Temperature ramp anneal





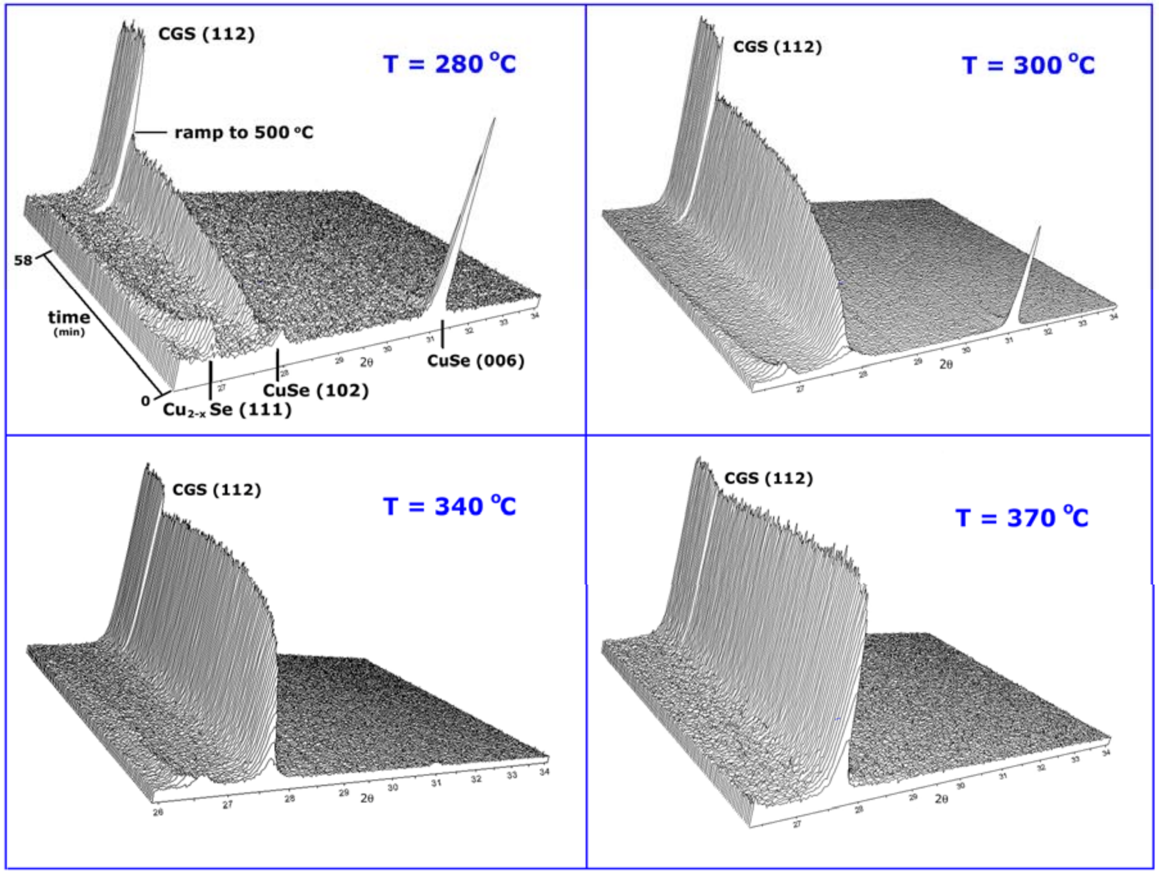
[Cu]/[Ga]=1.02

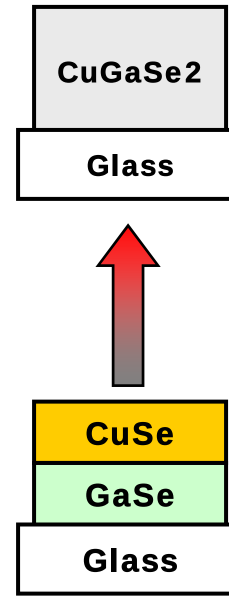
[Se]/[Cu+Ga]=0.97

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

amorphous

Isothermal annealing





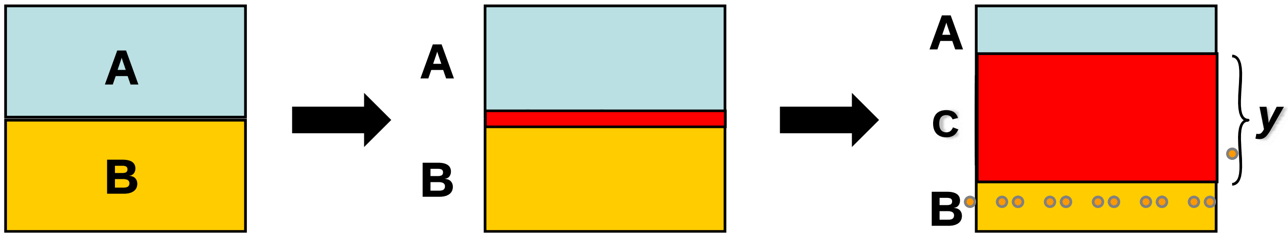
Assumption:

➔ Maximum peak area = 100 % reaction

➔ Normalized peak area = fractional reaction

Solid-state Growth Models

- **Parabolic growth model**

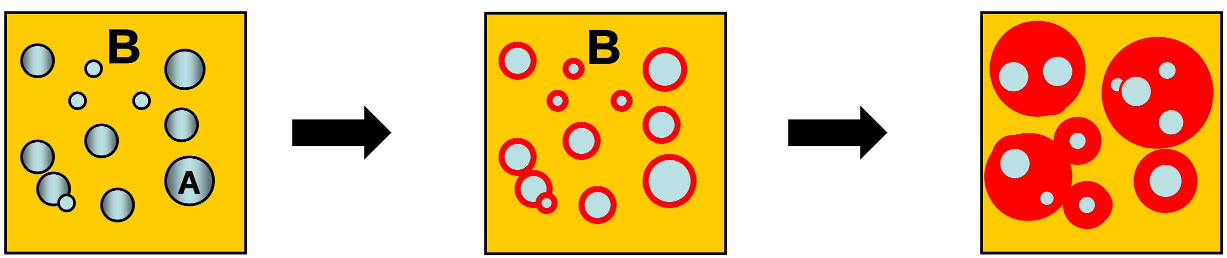


Before reaction | Nucleation at A-B interface | Diffusion thru product & reaction (ex. $D_{BC} > D_{AC}$)

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

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

- **Avrami growth model**



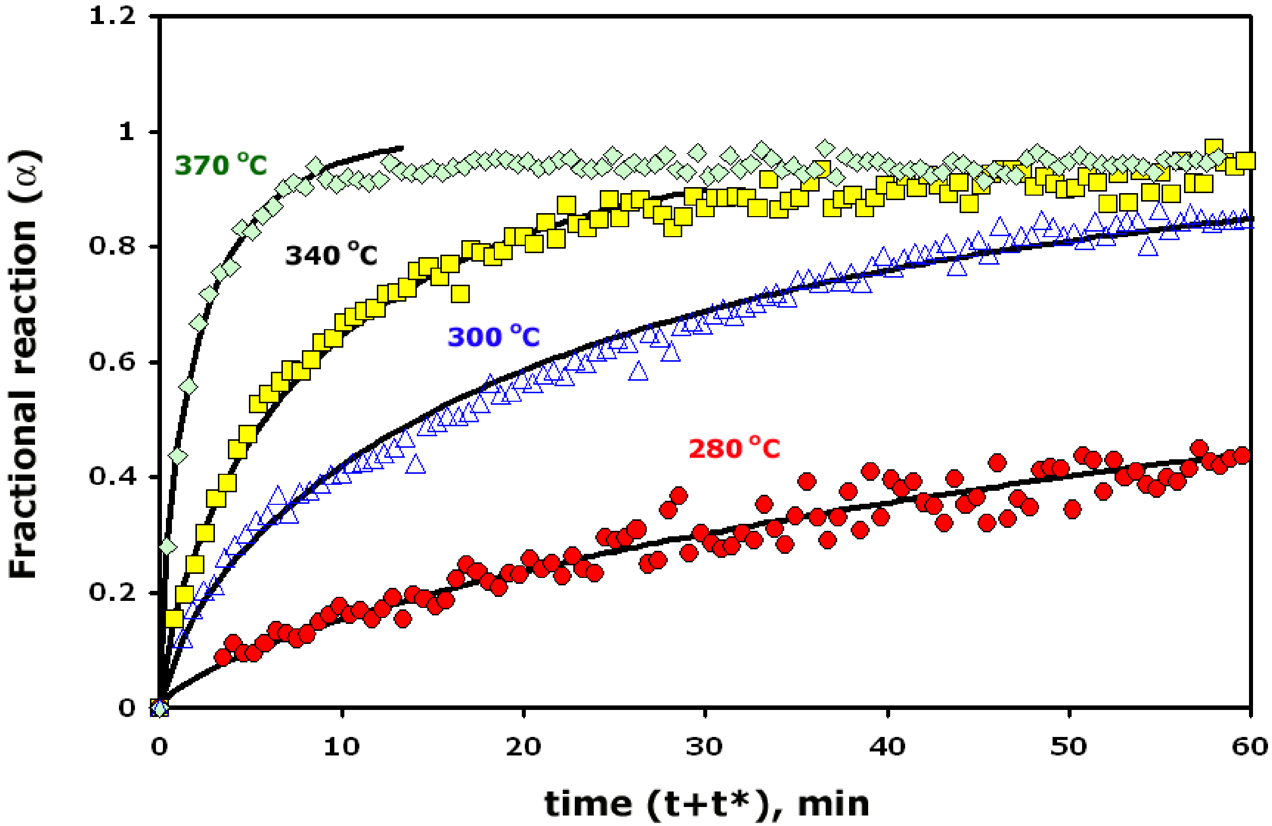
Phase A Covered with B | Nucleation | Diffusion & growth

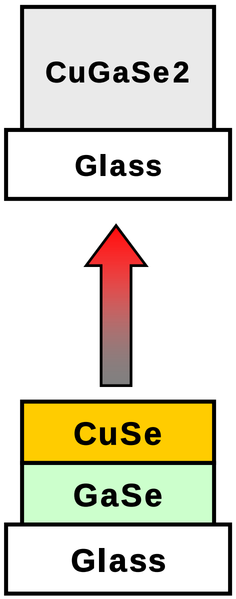
$$x = 1 - \exp[-(kt)^n]$$

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

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

Modified Avrami Analysis

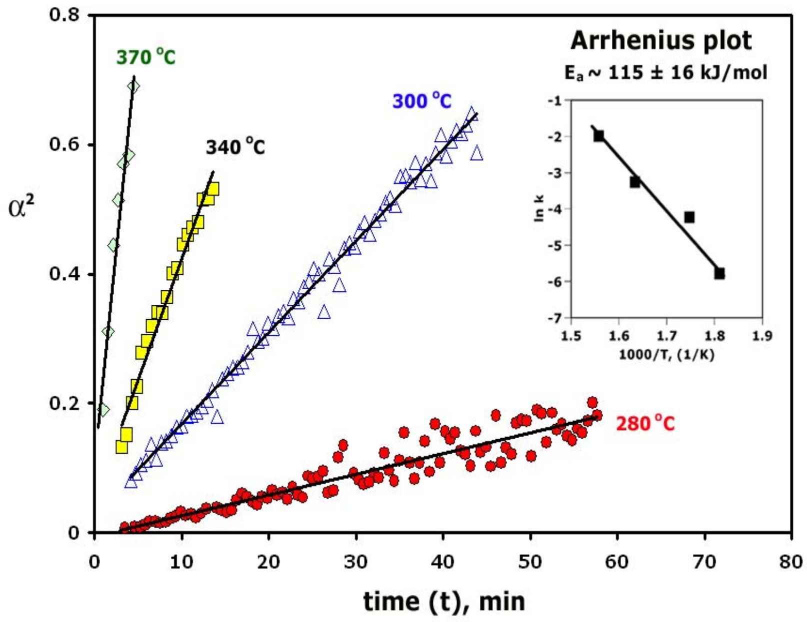




$$\alpha = 1 - \exp[-(k(t+t^*))^n]$$

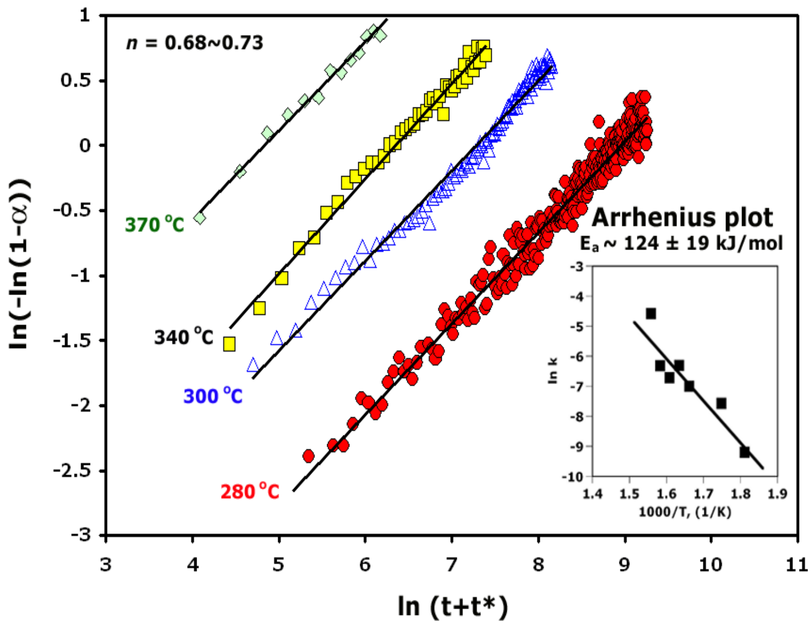
Kinetic Analysis

Parabolic model



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

Modified Avrami model

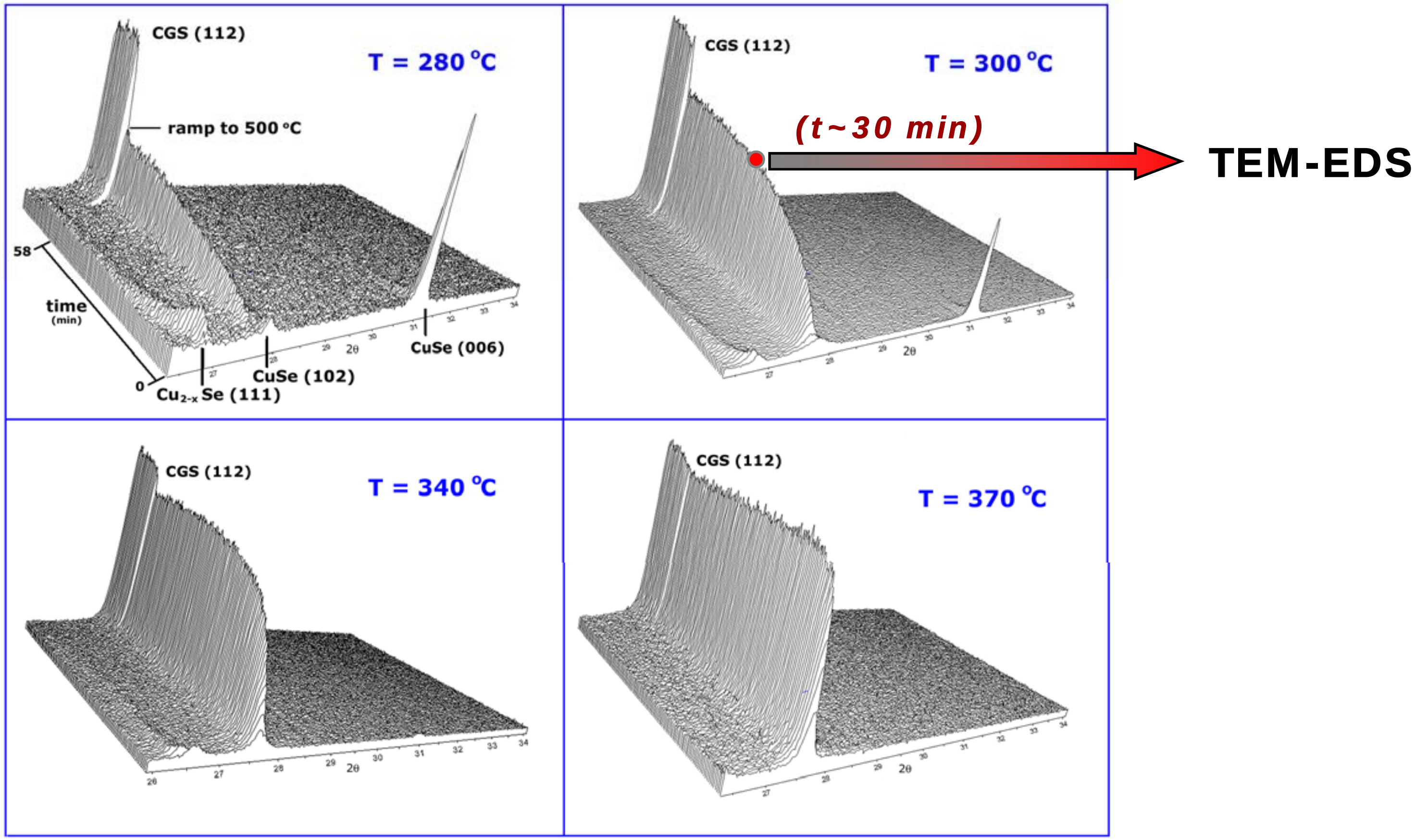


$\ln[-\ln(1-\alpha)] = n\ln(t+t^*) + n\ln k$

➔ *Analysis suggests one-dimensional diffusion controlled reaction*

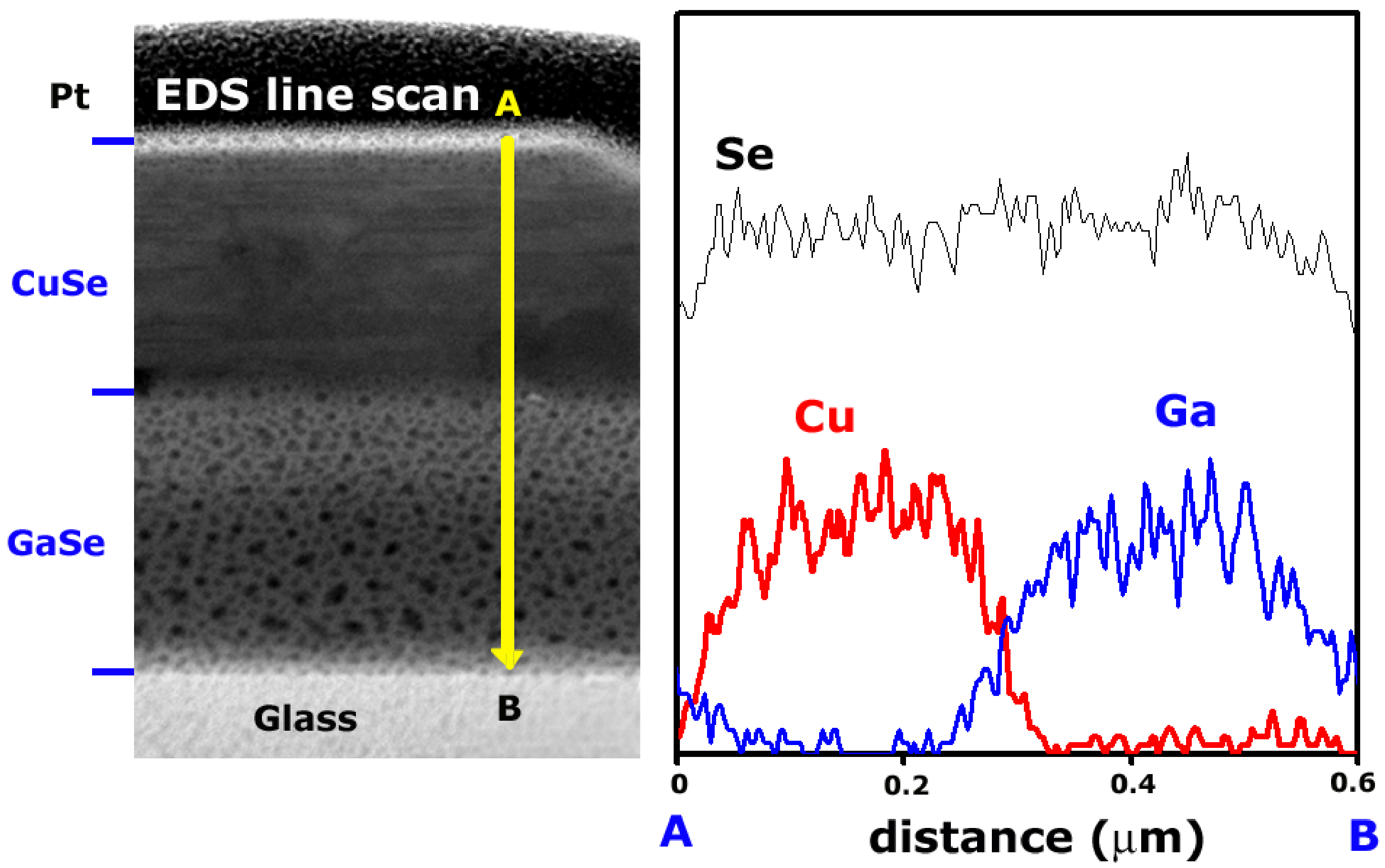
TEM-EDS

Isothermal annealing



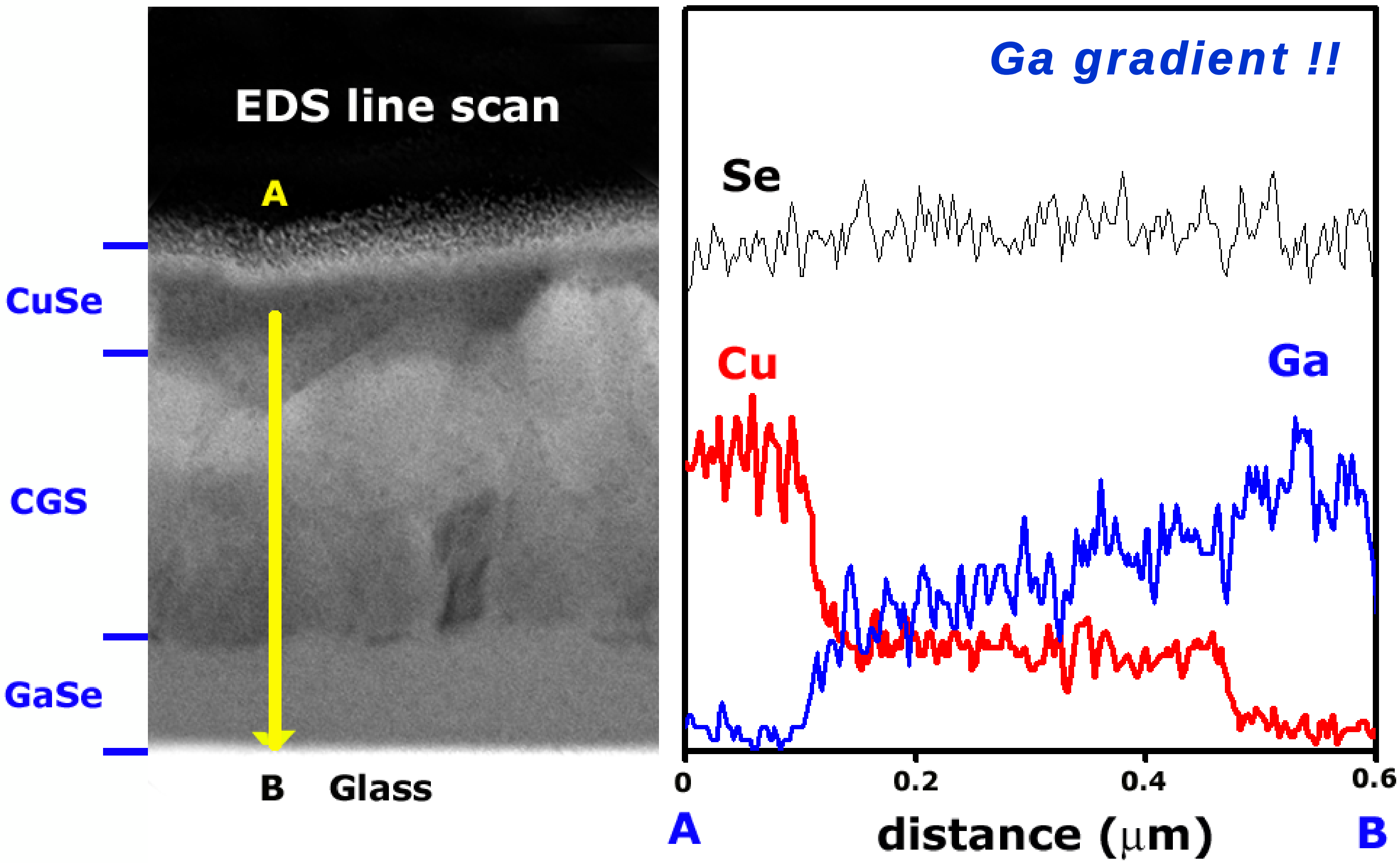
TEM-EDS Analysis

Glass / GaSe / CuSe Precursor

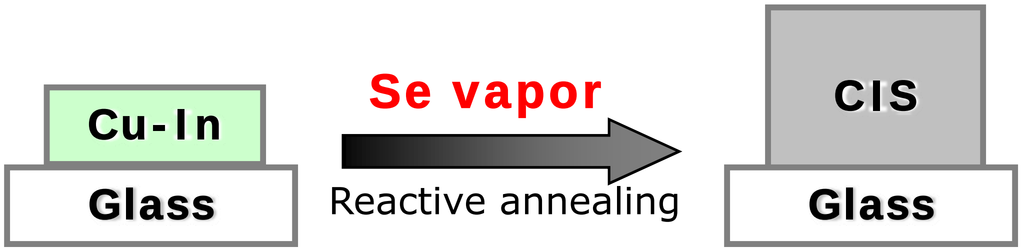


TEM-EDS Analysis

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

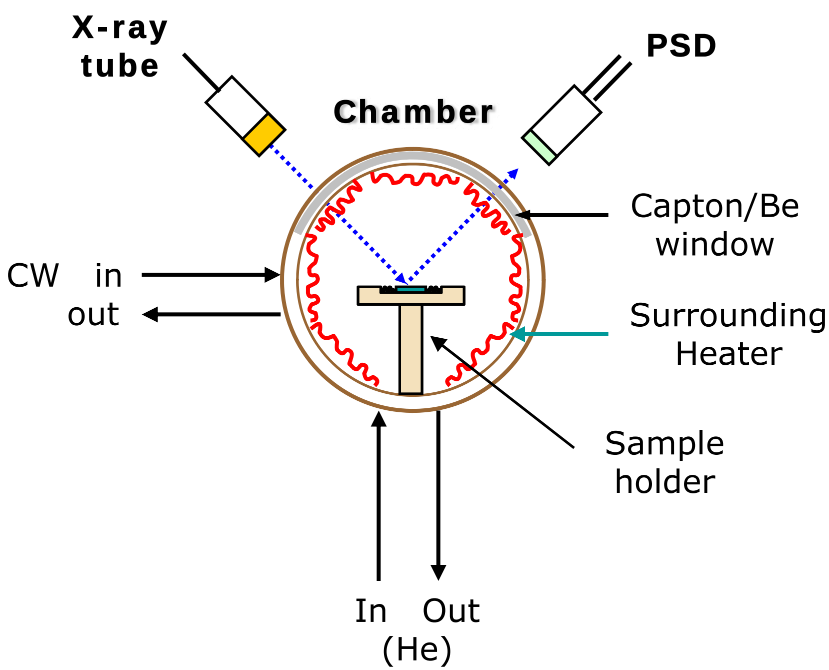


$CuInSe_2$ formation from selenization of Cu-In precursor

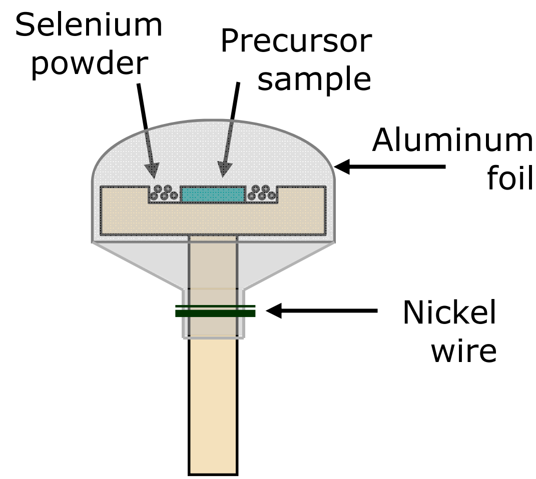


HT-XRD with Selenization Chamber

Panalytical Philips X'pert system



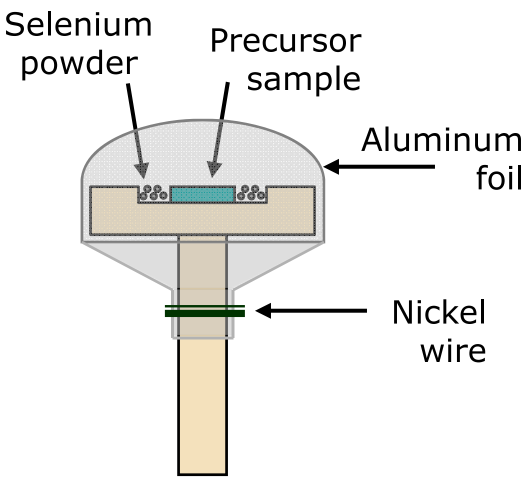
Sample holder



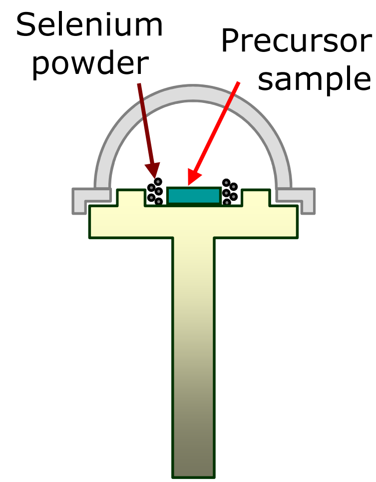
➔ ***High Temperature Materials Laboratory, ORNL***

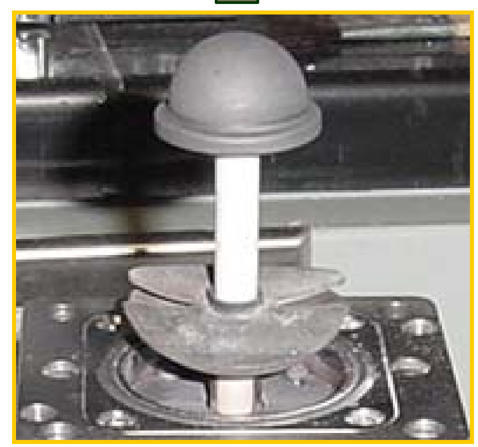
Selenization Chamber

Aluminum foil



Graphite dome



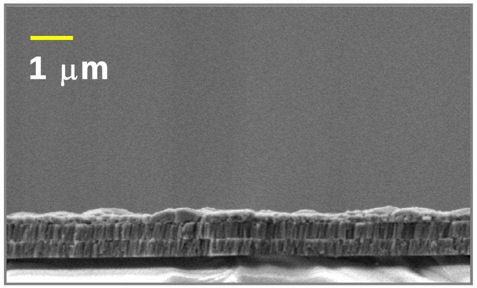


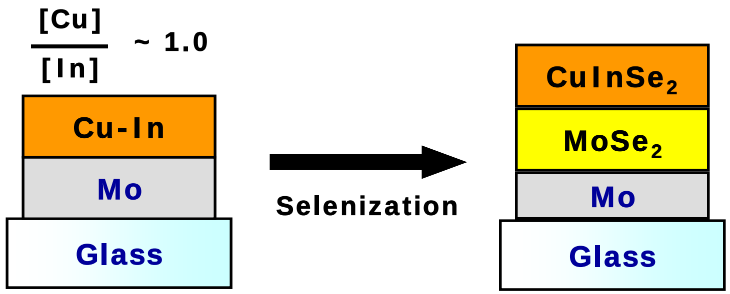
- **Al foil :**
  - **(1) Loss of X-ray intensity**
  - **(2) Possible reaction with Se above 650°C**
- **Graphite dome :**
  - **(1) Easy to handle**
  - **(2) Extremely X-ray transparent**
  - **(3) High stability**

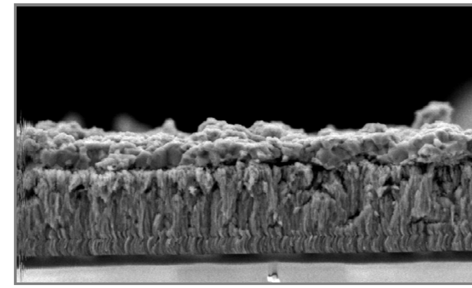
SEM / EPMA

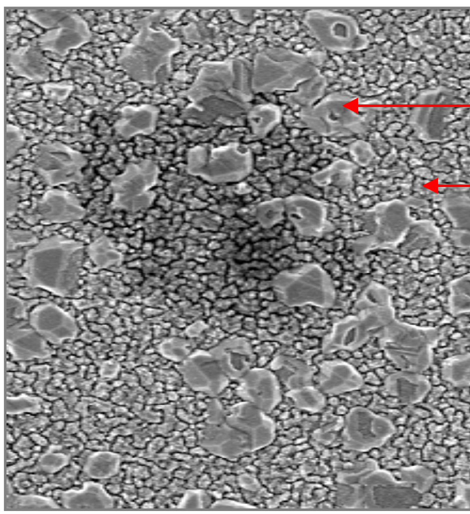
Precursor

Selenized CIS



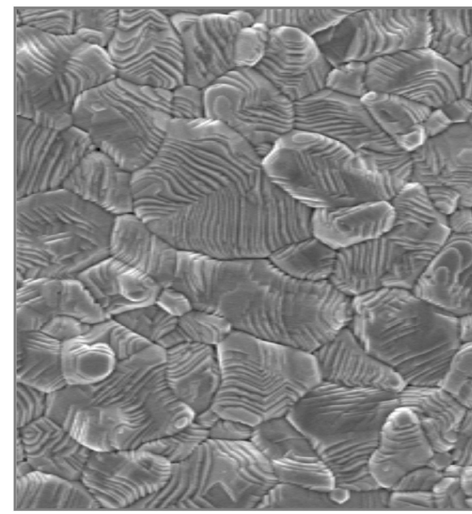






Island (In-rich)

Matrix (Cu_2In+ CuIn)



EPMA Results (Va=6 keV)

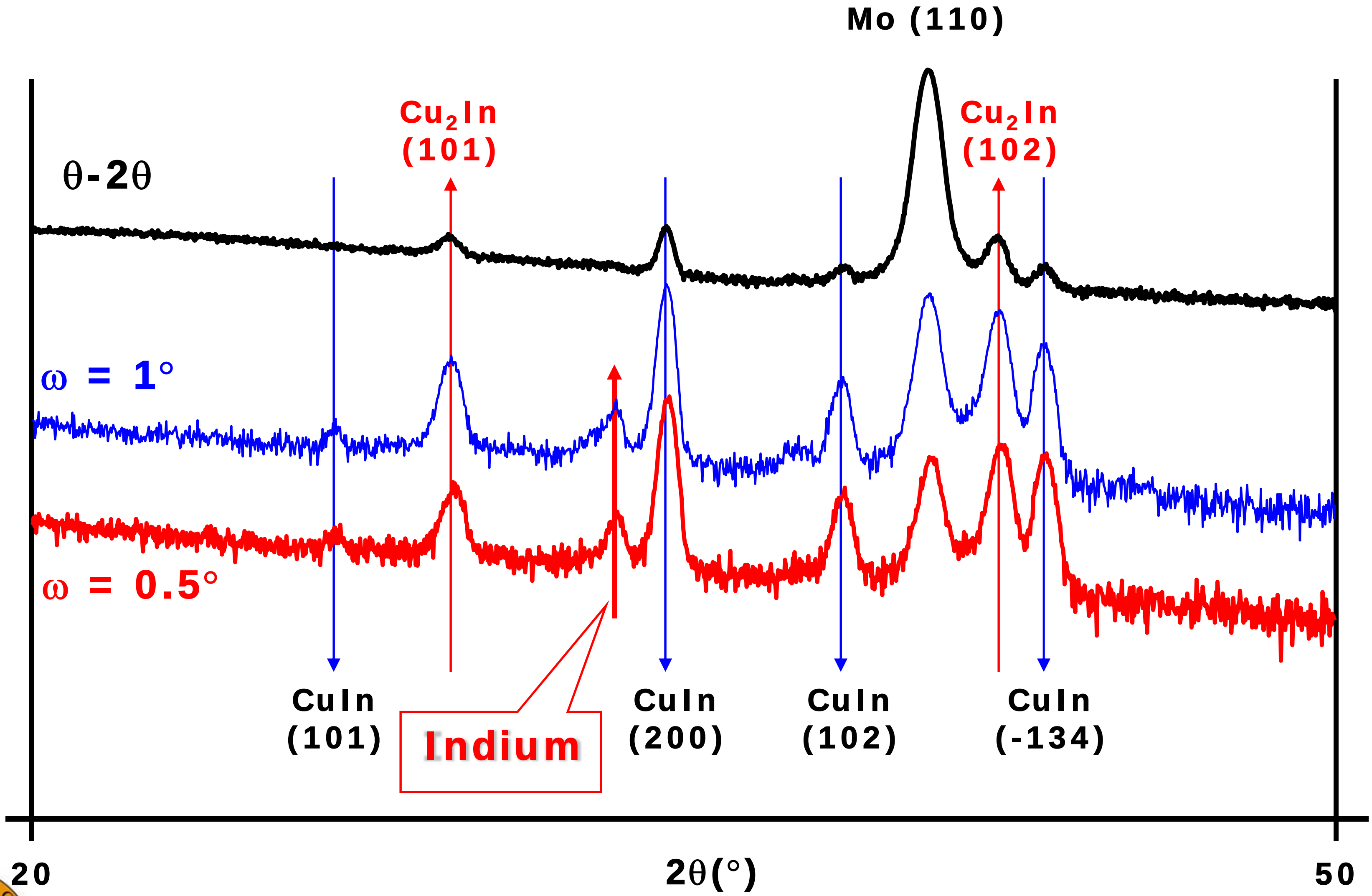
	Matrix	Island
Cu (at.%)	59.4 (±1.2)	36.0 (±1.0)
In (at.%)	40.6 (±1.2)	64.0 (±1.0)

1 μm

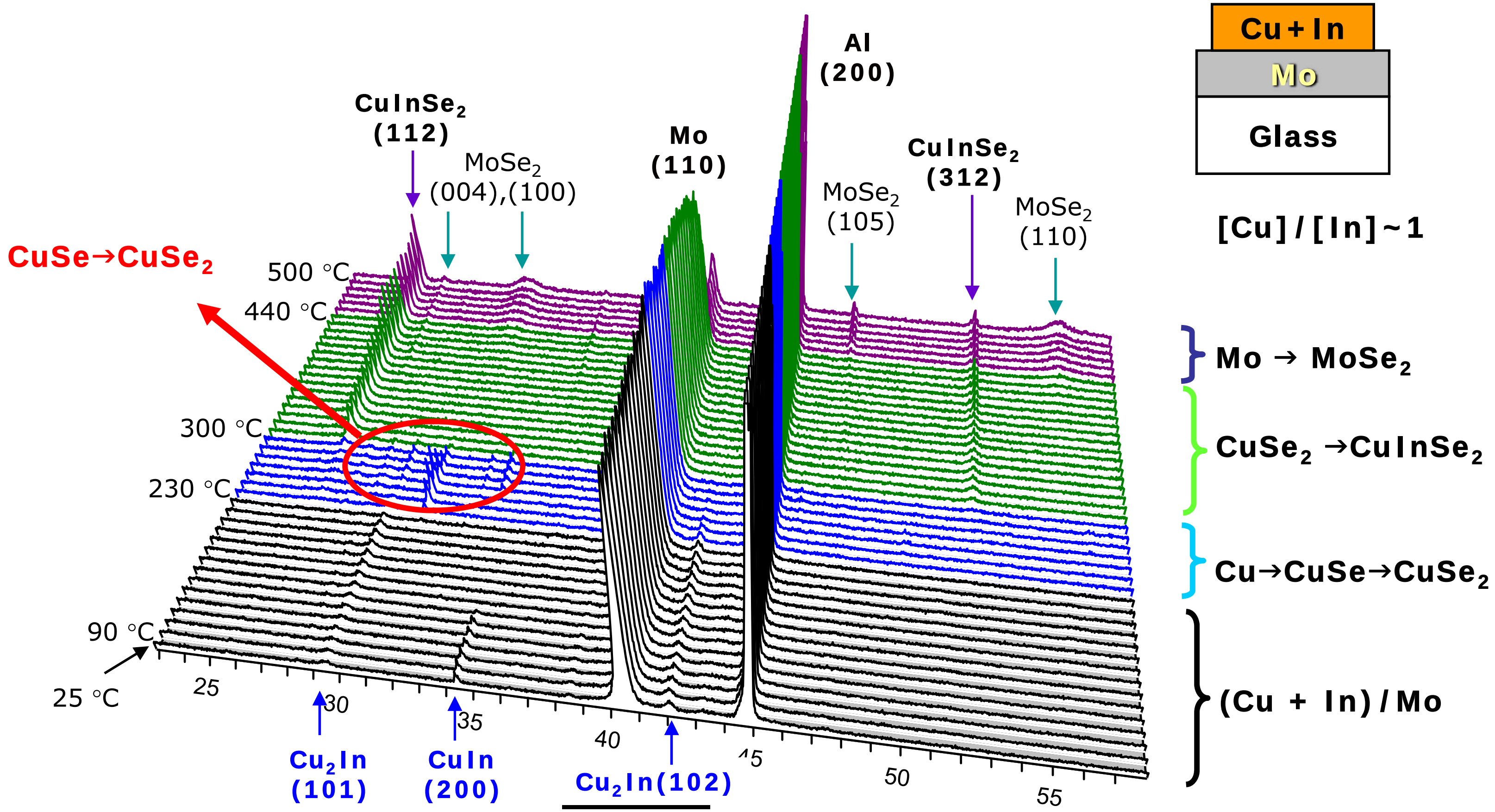
▸ **Island : In-rich or nearly pure indium phase**

1 μm

XRD & GI-XRD for Precursor

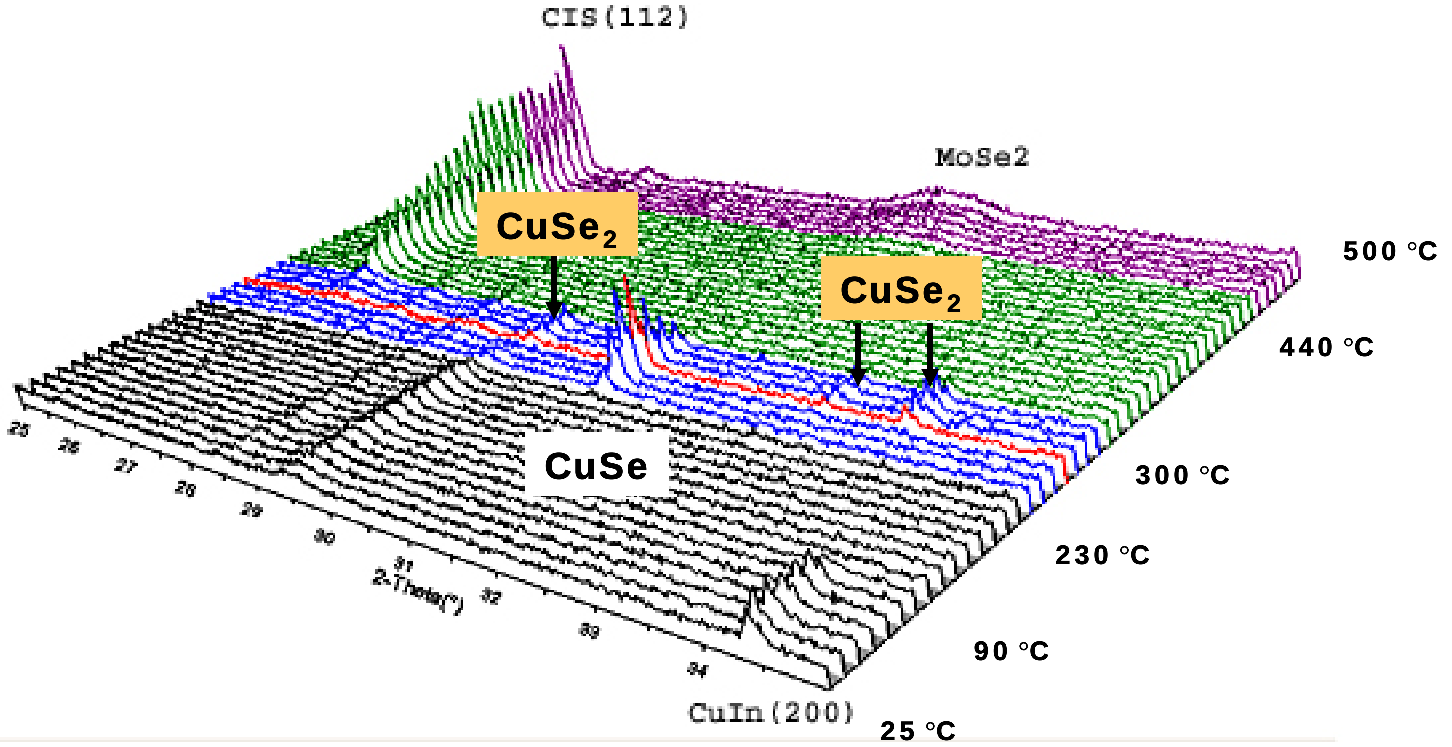


(Cu+In)/Mo Selenization



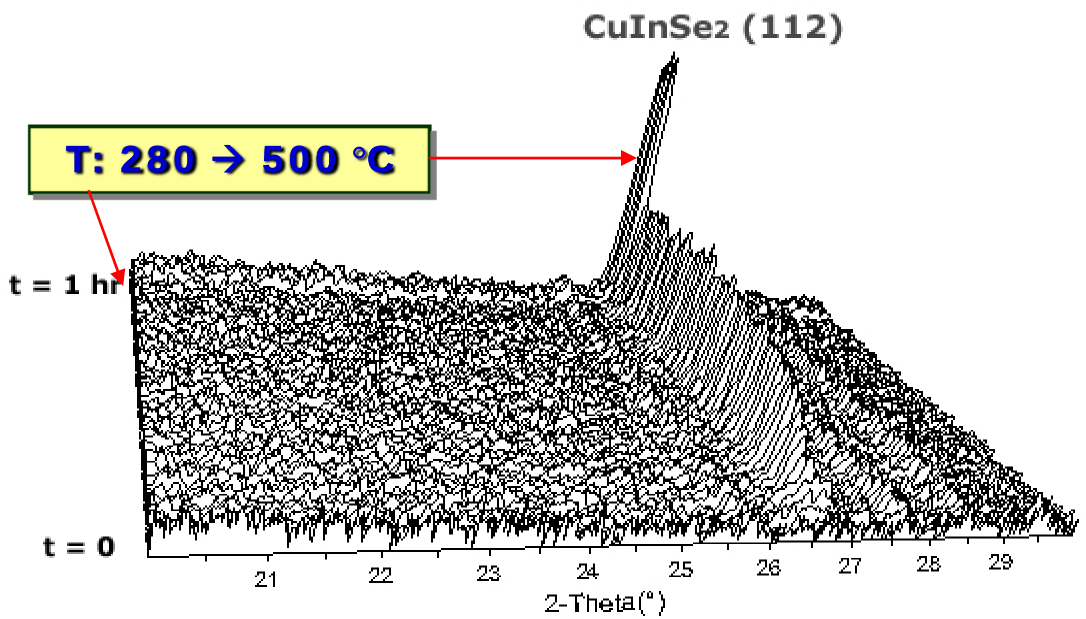
(Cu+In)/Mo Selenization

Cu/In → CuSe → $CuSe_2$ → $CuInSe_2$



Isothermal Selenization

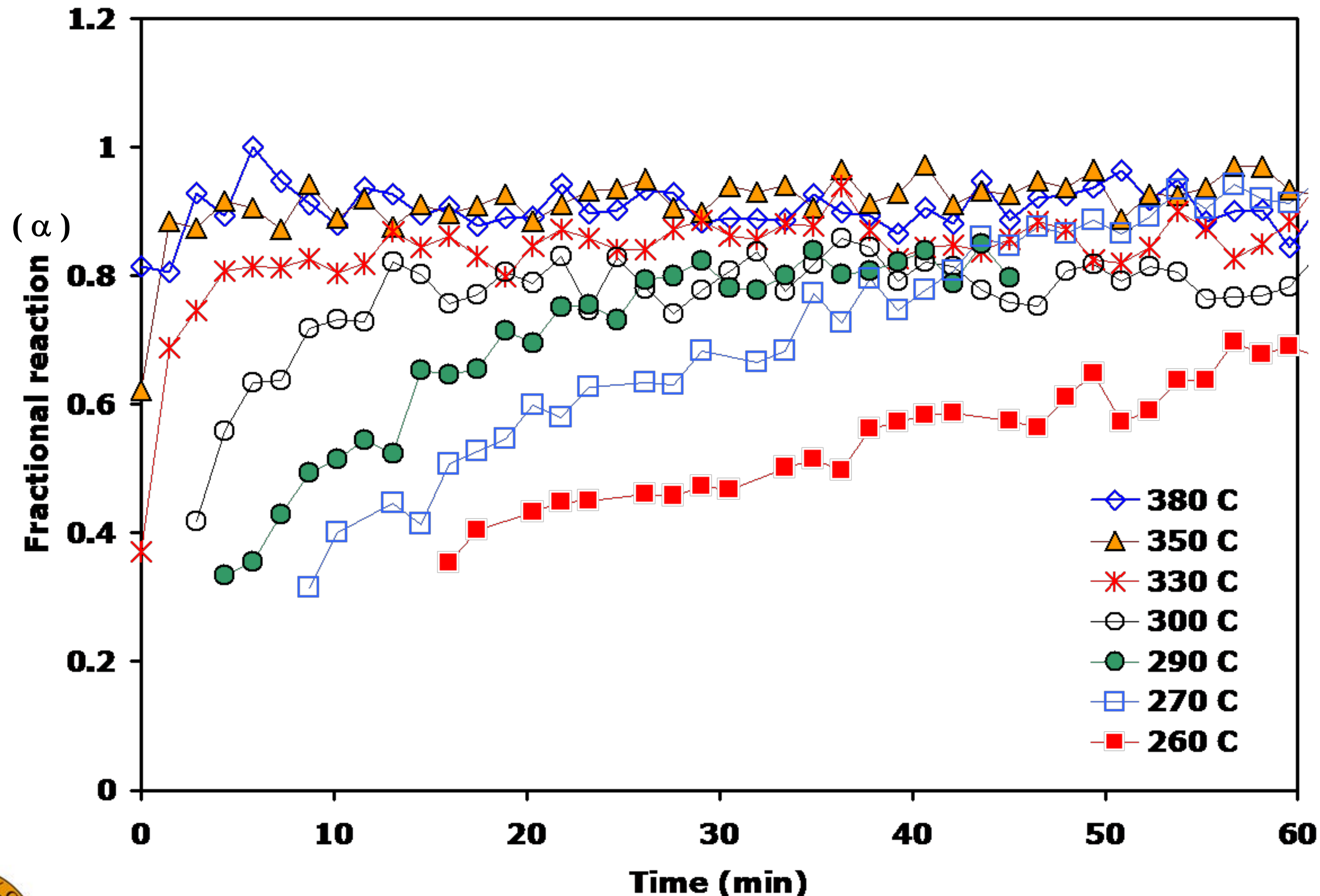
Temperature = 280 °C



■ Assumption for kinetic analysis

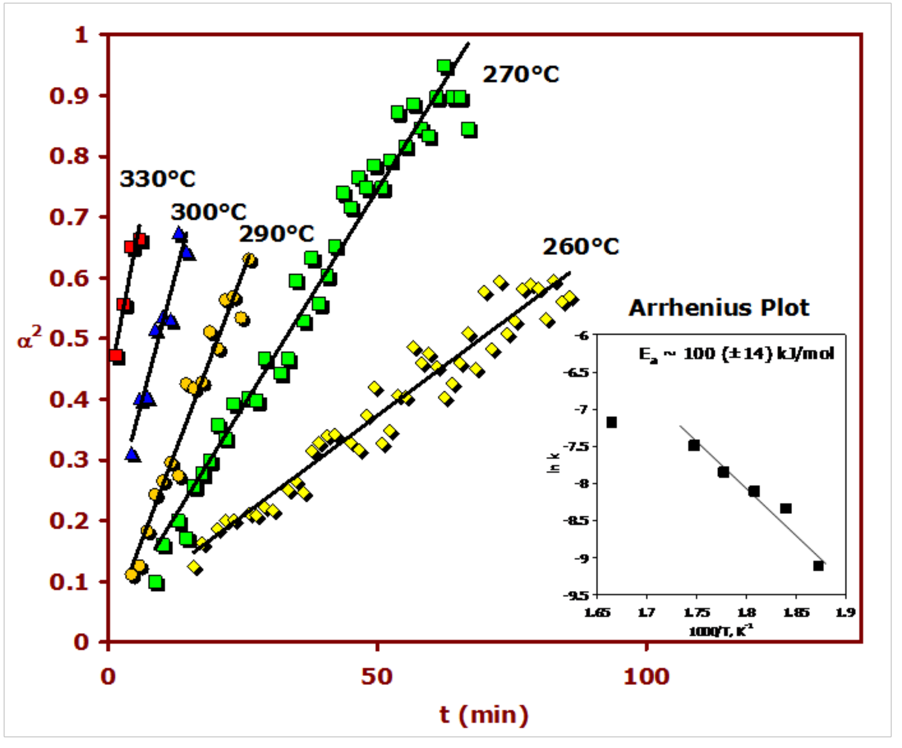
➔ **Largest peak area = 100 % reaction**
➔ **Fractional reaction = normalized peak area**

Fractional Reaction



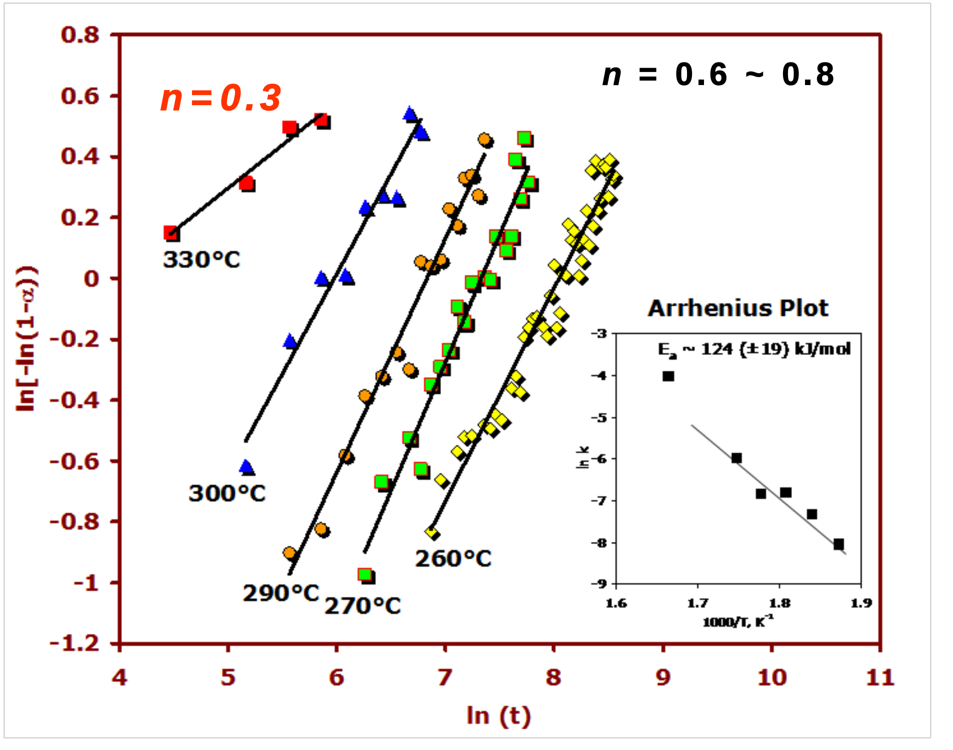
Kinetic Analysis

Parabolic model



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

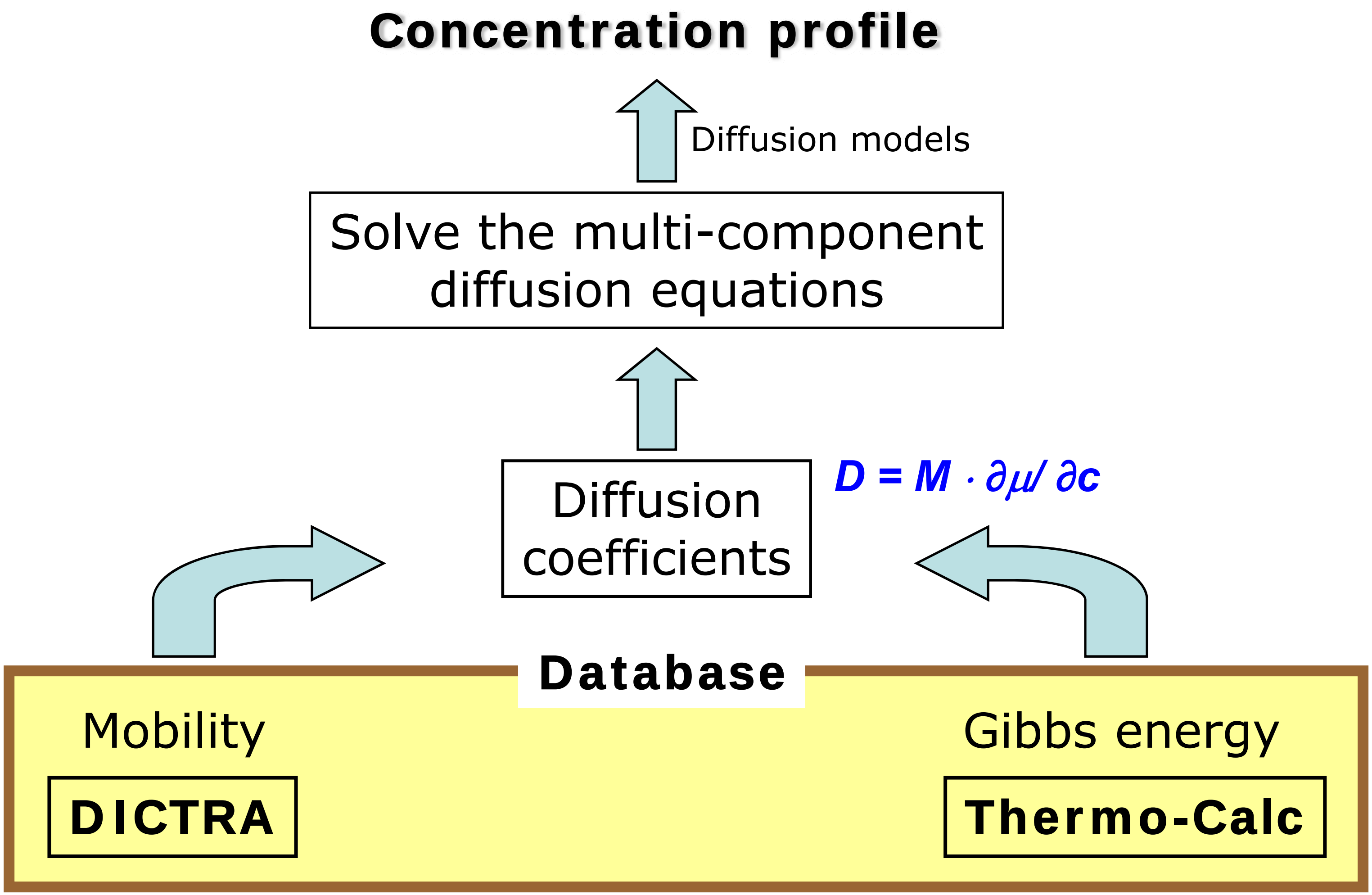
Avrami model



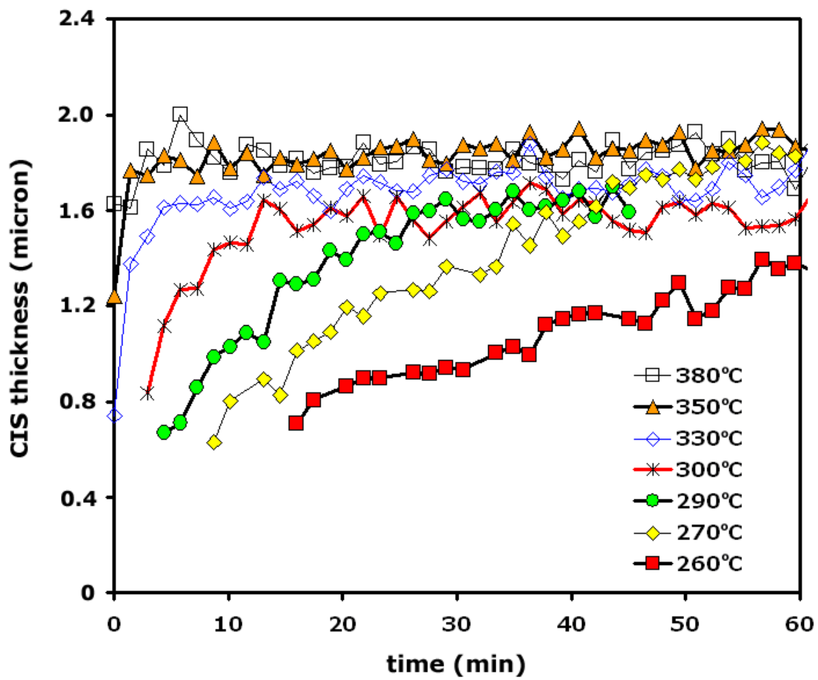
$\ln[-\ln(1-\alpha)] = n\ln(t) + n\ln k$

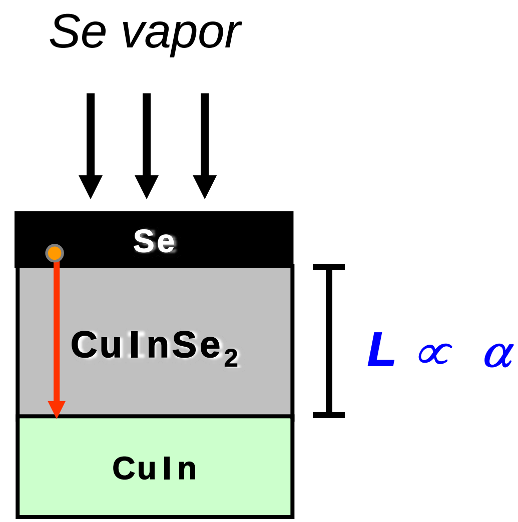
➔ *Analysis suggests one-dimensional diffusion controlled reaction*

DICTRA Modeling



DICTRA Optimization



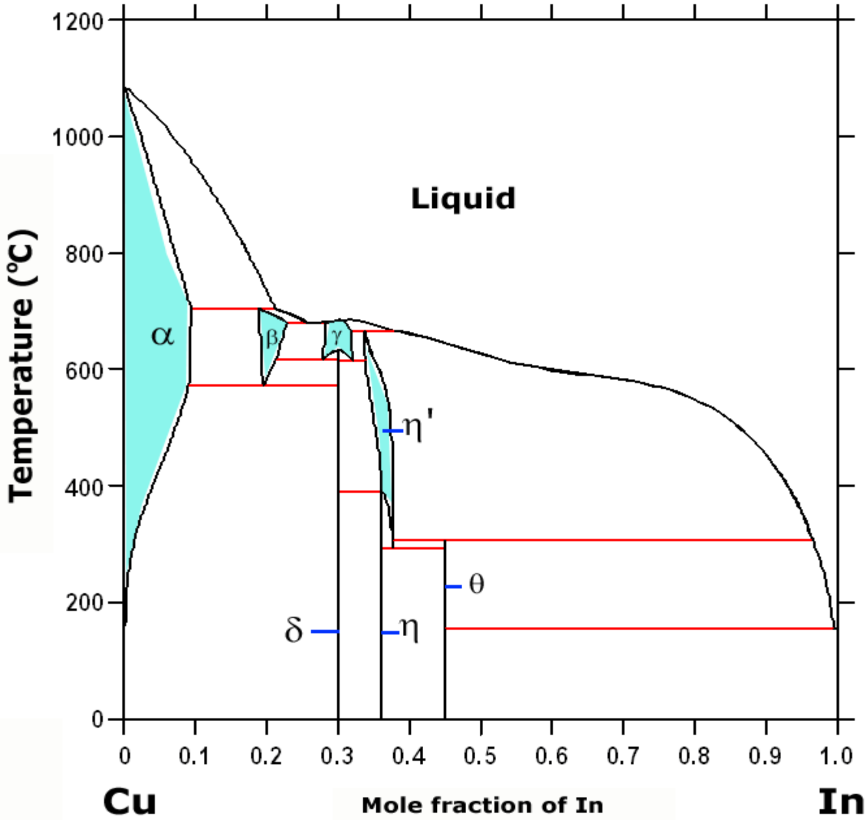


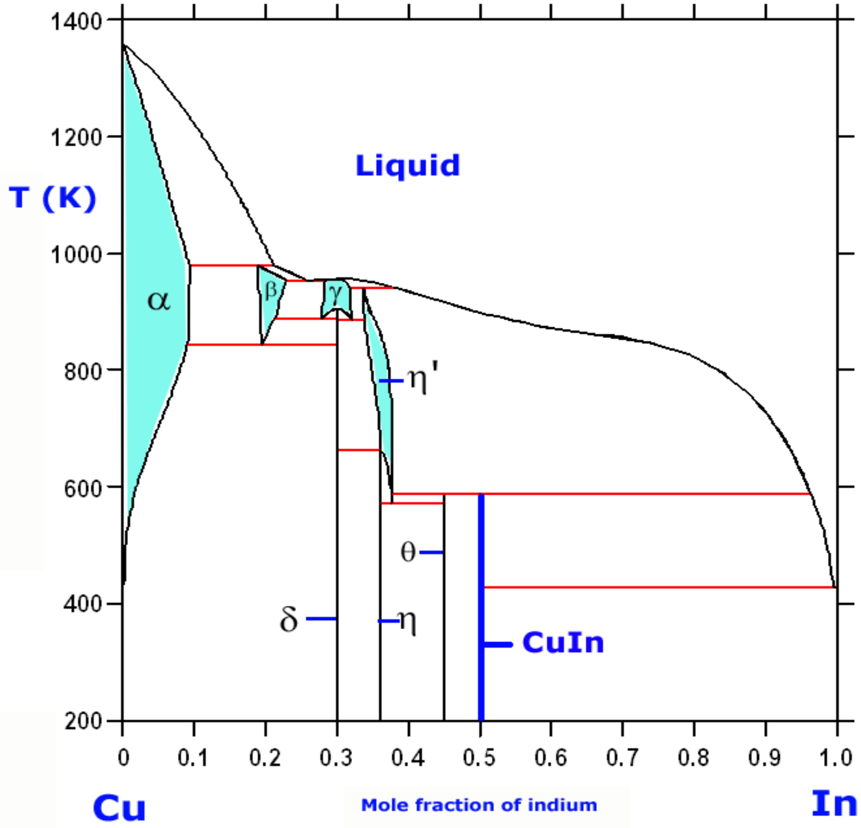
Assumption:

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

Instead of: $m Cu_2In + n CuIn + m In + (4m+2n) Se \rightarrow (2m+n) CuInSe_2$

Cu-In Thermodynamic Database





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

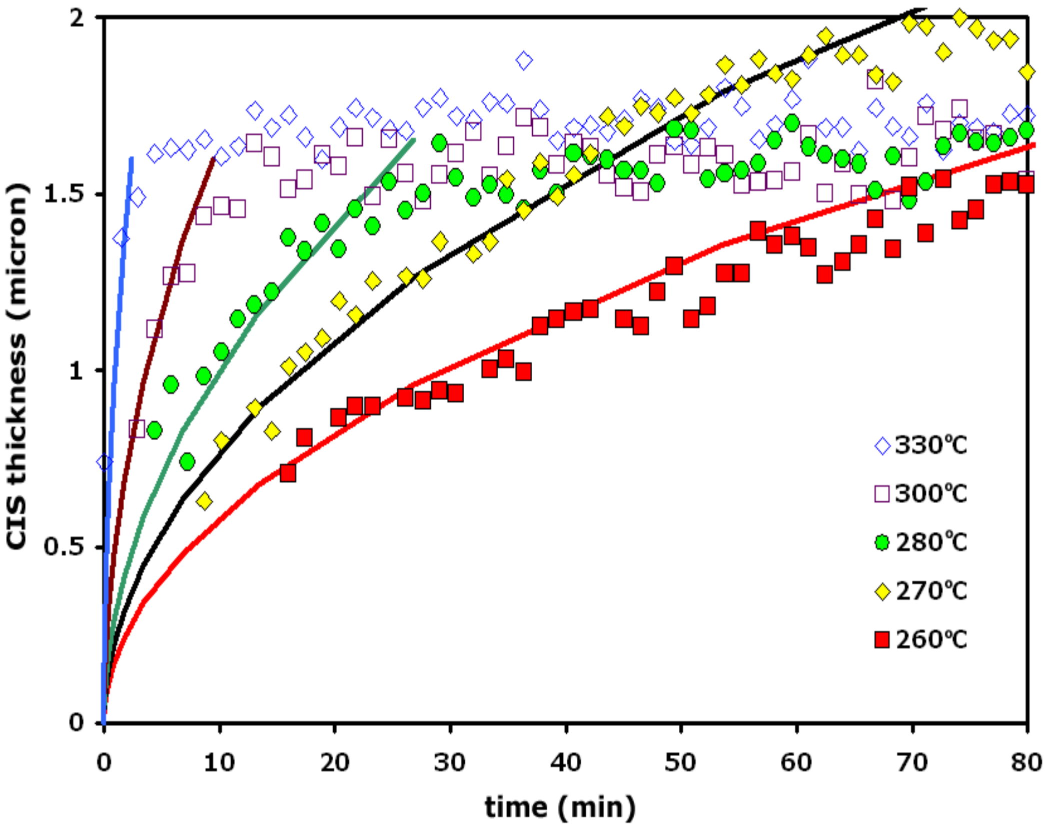
DICTRA Optimization Results

Mobility parameter in DICTRA

$MQ = -Q_B + RTln(M_B^0)$

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.