Routes for Rapid Synthesis of $CuIn_xGa_{1-x}Se$ Absorbers

R. Krishnan, W. K. Kim, S. Kim, C.H. Chang, M. Ider, B.J. Stanbery, O.D Crisalle, J. Shen, E. A. Payzant, V. Craciun, C. Campbell, and T. J. Anderson

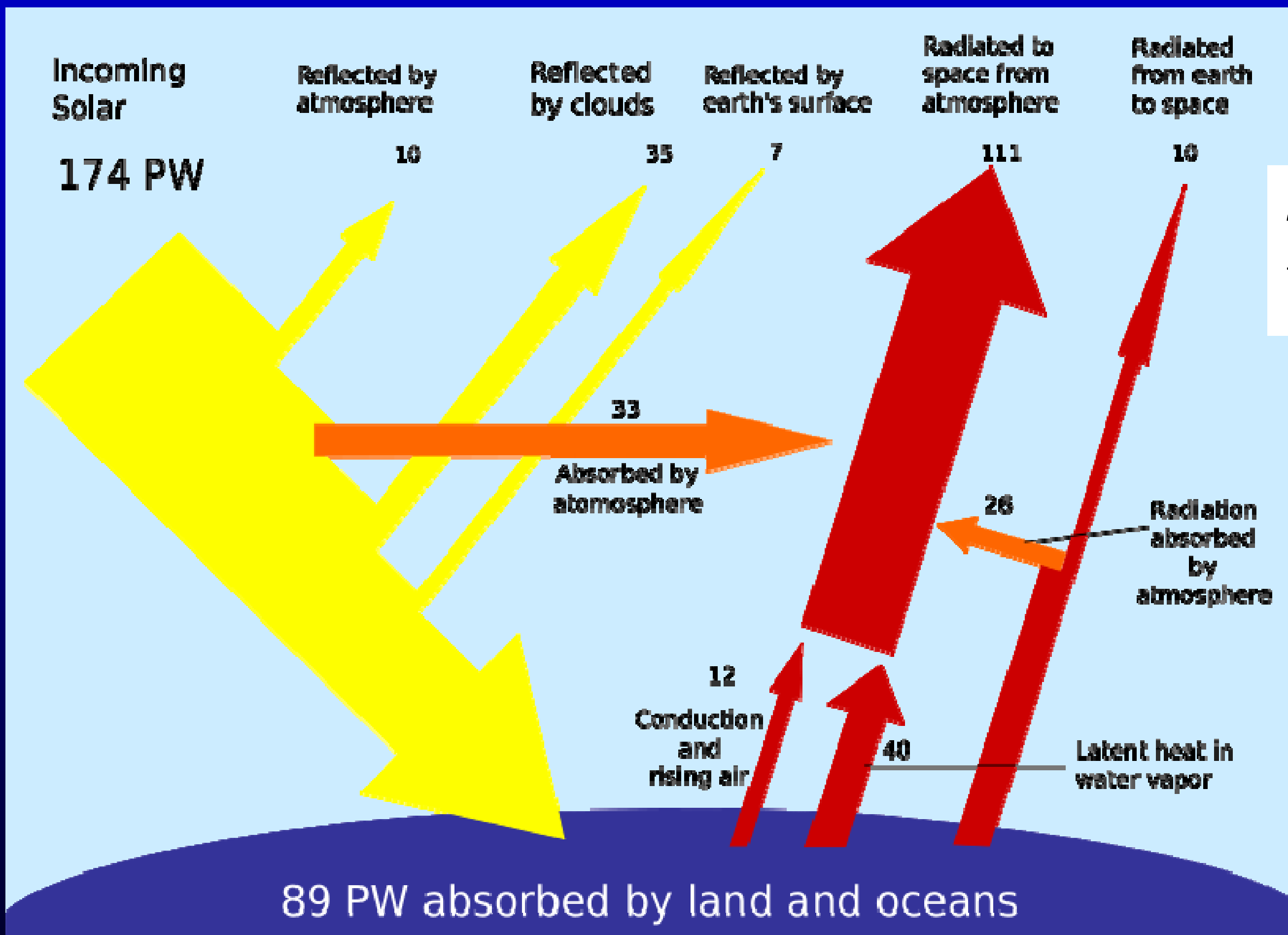
Why Should We Build Solar Cells?

Why do you rob banks, Willy?

"Cause that's where the money is!"

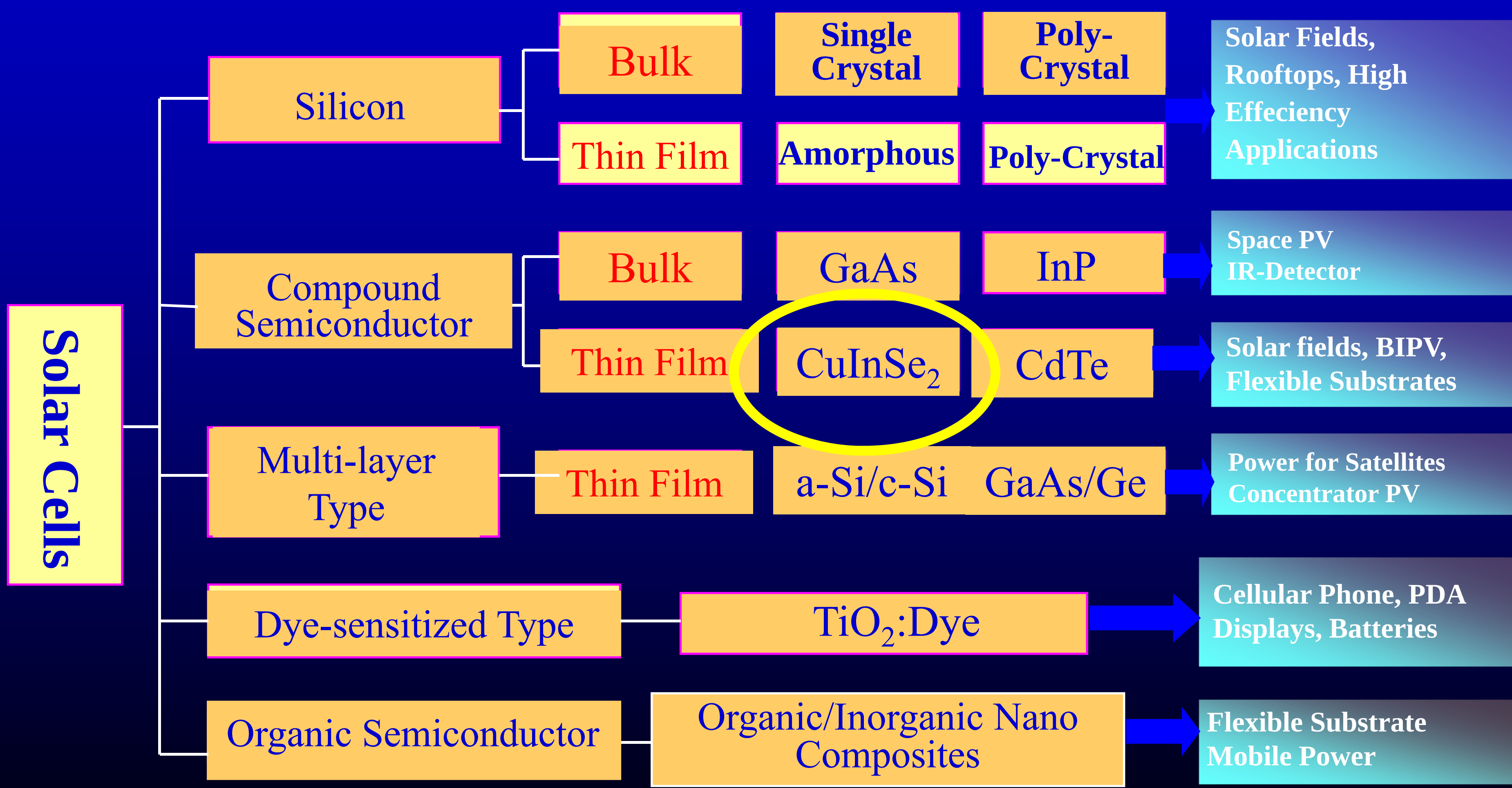
Willy Sutton
Bank Robber

Because That Is Where the Energy Is!



~0.015 PW Used by Humans

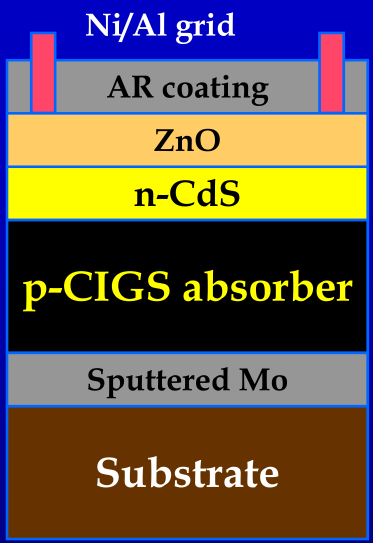
Classification of Solar Cells



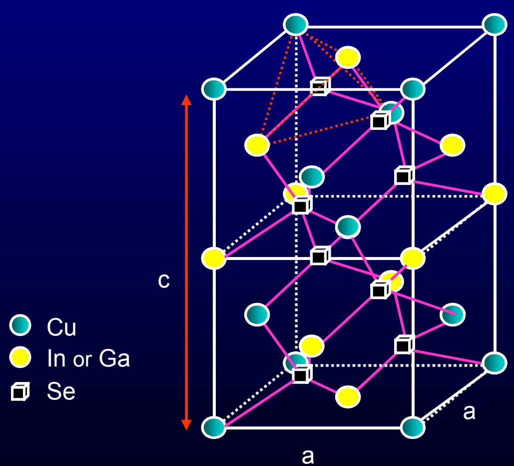
$Cu(In_{1-x}Ga_x)Se_2$ Solar Cells

Most Promising Thin Film Absorber Material

- Direct band gap (Eg ~ 1.2 eV)
- High optical absorption coefficient: ~ 2 µm
- High radiation resistance
- High reliability
- Lower cost per Watt installed
- High conversion efficiency: cell: 20% and module: 13%
- Efficient in low-angle & low-light conditions
- Flexible substrates possible (BIPV, cheaper substrates?)
- Positive response under concentration



CIGS solar cell structure

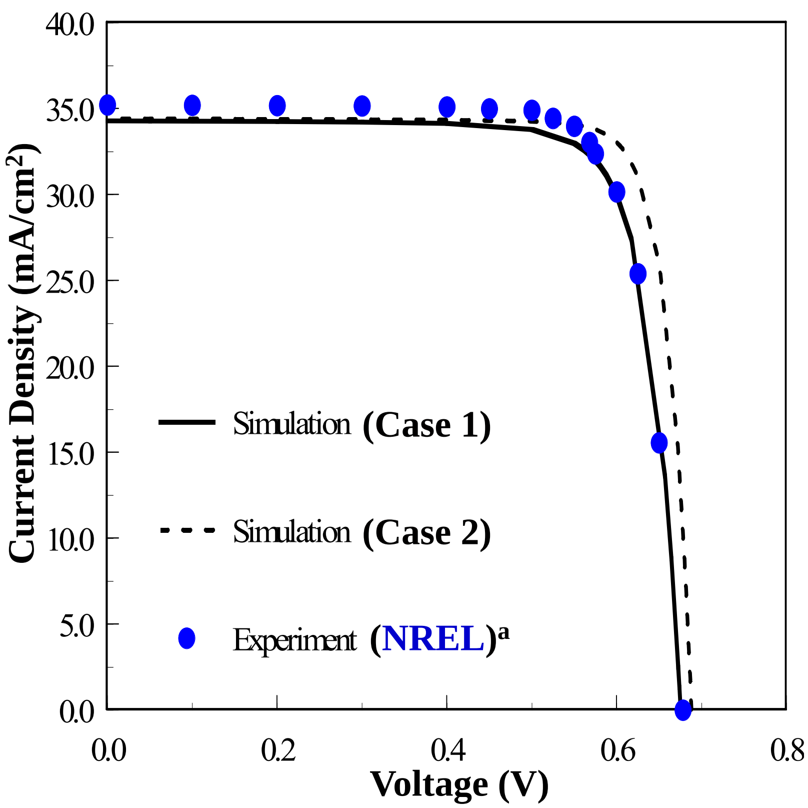


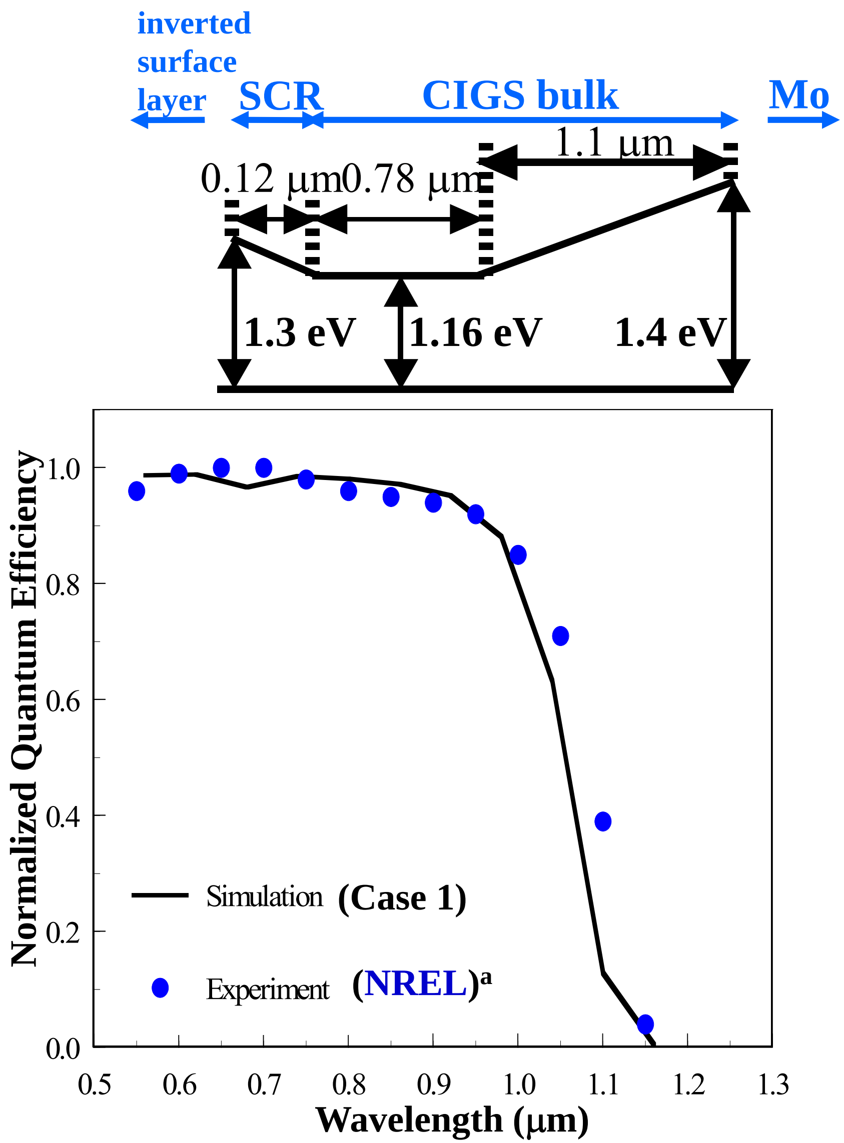
Chalcopyrite structure

Key Issue: Cost Reduction - $\$/W_p$

- **Materials Costs (~50%)**
  - Material efficient deposition
  - Lower substrate cost (e.g. BIPV)
    - » Lower temperature
- **Processing Costs**
  - Capitalization largest cost
    - » Process intensification
    - » Increase process yield (e.g., process control)
    - » Increase throughput (e.g., scale-up, reduce absorber thickness, high rate deposition/rapid reaction pathway/lower temperature)
- **Increase Cell Efficiency**
  - For advanced technologies: Module level < Champion cell ~ Predicted

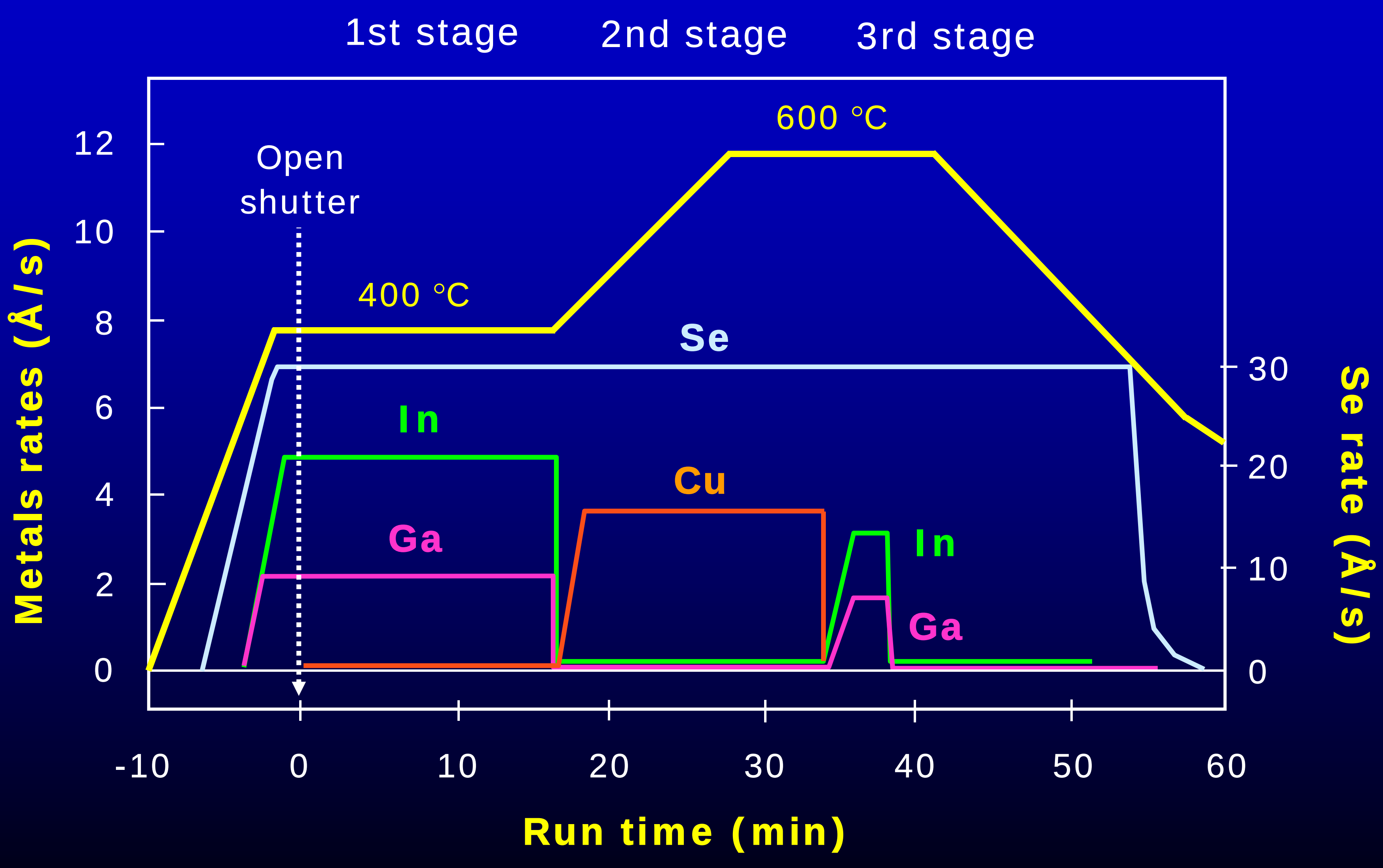
Comparison of Simulated and Reported *Photo- J-V* and Quantum Efficiency



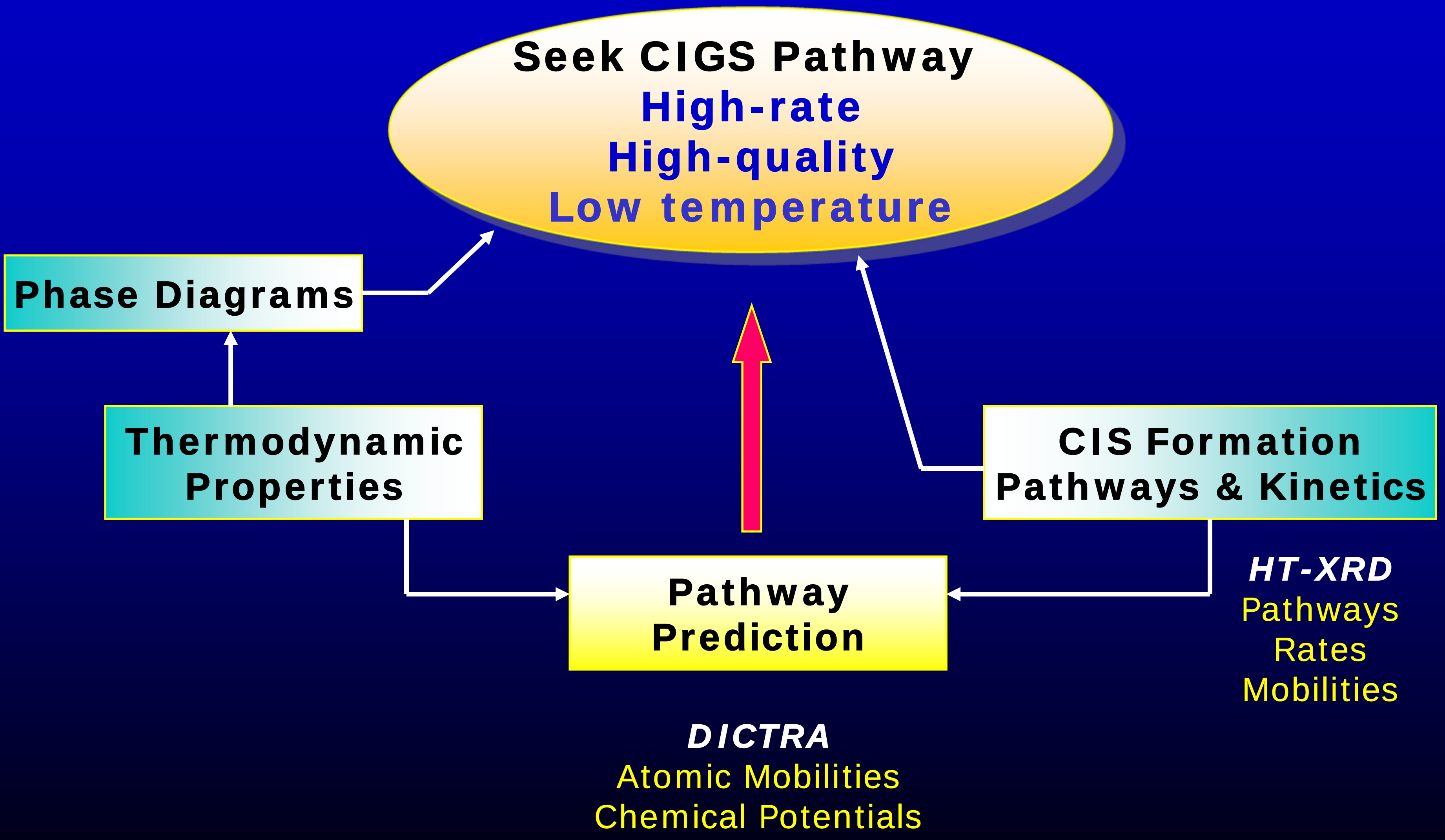


[a]M.A. Contreras *et al*., **18.8%** CIGS cell

NREL 3-stage Process: Champion Cell



Approach


Seek CIGS Pathway
High-rate
High-quality
Low temperature
Phase Diagrams
Thermodynamic Properties
CIS Formation Pathways & Kinetics
Pathway Prediction
HT-XRD
Pathways
Rates
Mobilities
DICTRA
Atomic Mobilities
Chemical Potentials

Approach to Developing Phase Diagrams

DATA → **Critical Evaluation, Model Selection & Assessment** → **Equilibrium Phase Diagrams**

Thermochemical & Equilibrium

Structure

Bulk & Point Defects

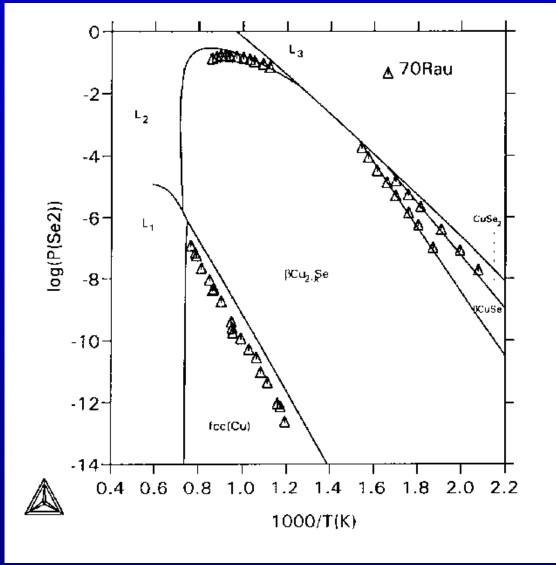
- Literature
- Measurements
  - **EMF, Equilibration**
- First Principles
- Estimation

Cu-Ga-In-Se System

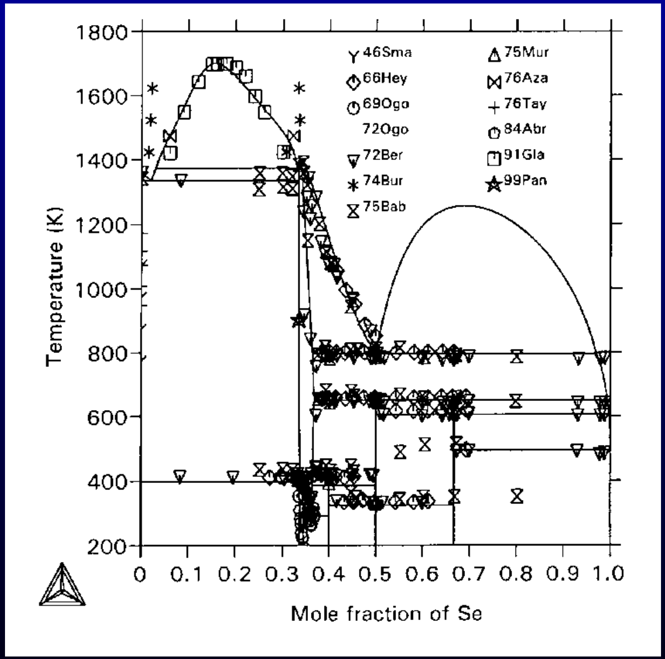
- **4 unary sub-systems**
- **6 binary sub-systems**
- **4 ternary sub-systems**

Comparison of Calculated Cu-Se Phase Diagram with Experimental Data

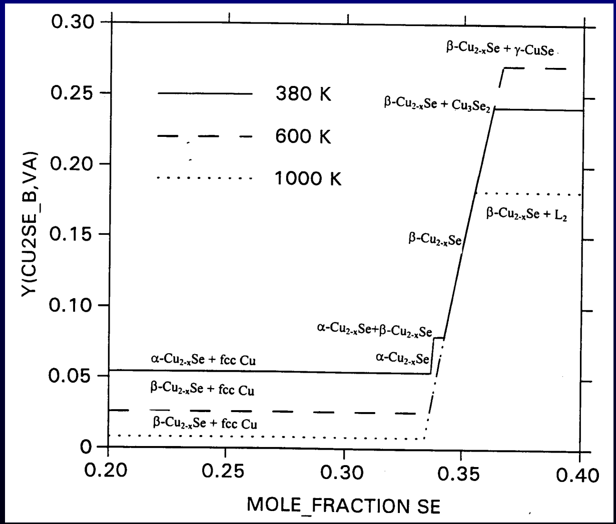
Phase	**Model**
Liquid	**Ionic two sub-lattice model**
	$(Cu+1,Cu+2)p(Se-2,Va,Se)q$
α-$Cu_{2-x}Se$	**Sub-lattice model (3 sub-lattices)**
	$(Cu,Va)_1(Se,Va)_1(Cu)_1$
β-$Cu_{2-x}Se$	**Sub-lattice model (3 sub-lattices)**
	$(Cu,Va)_1(Se,Va)_1(Cu)_1$
Fcc (Cu)	**Regular solution model**



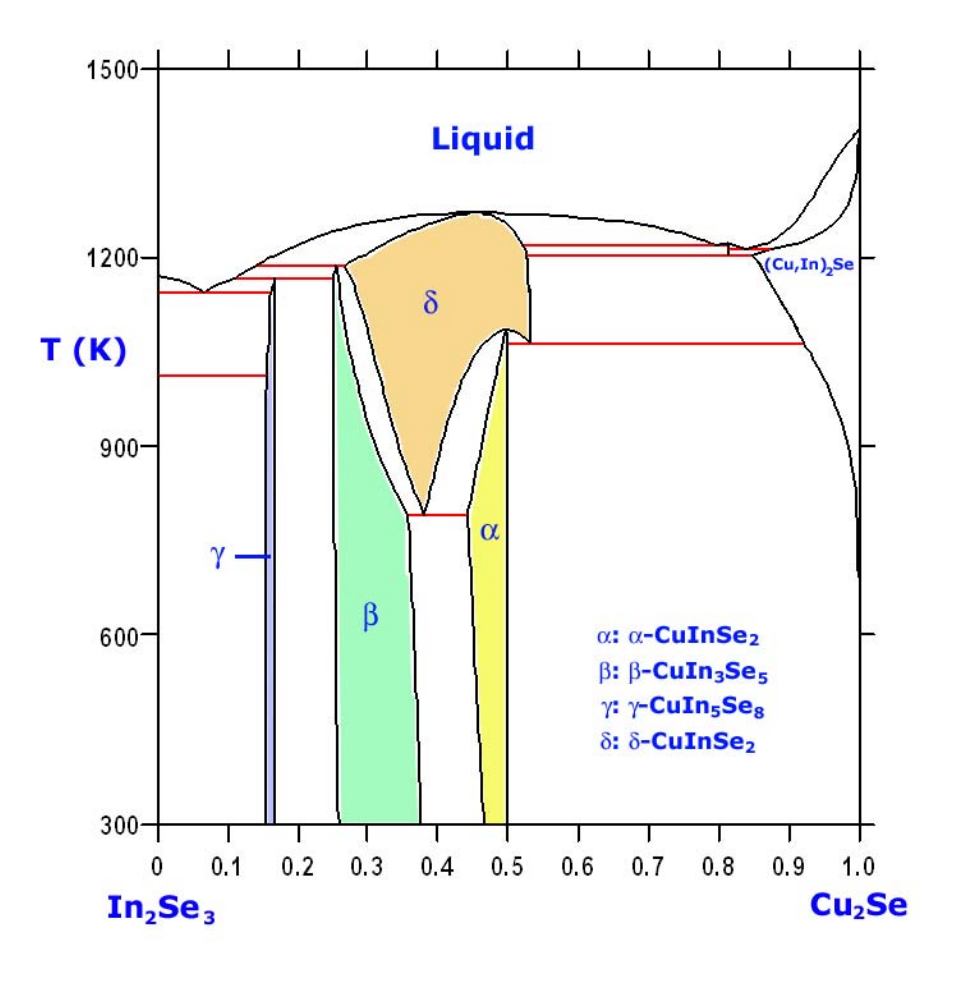
Se$_2$ Partial Pressure



V$_{Cu}$ in $Cu_{2-x}Se$

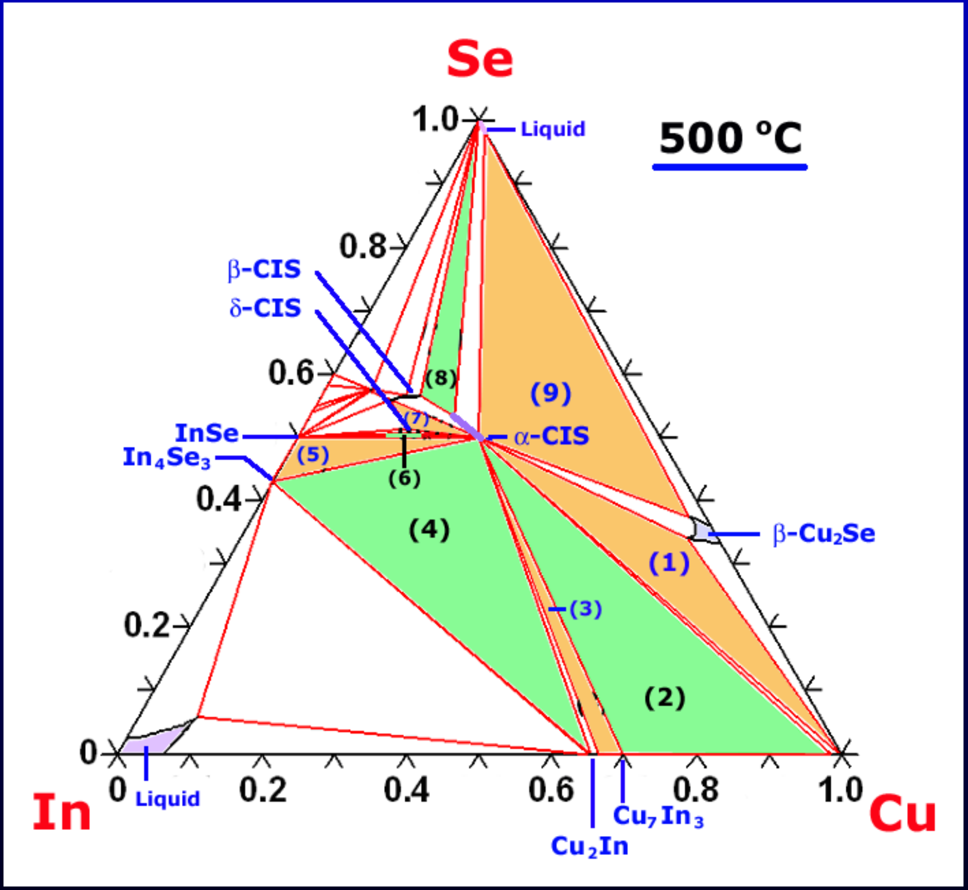


Isopleth In_2Se_3-Cu_2Se of Cu-In-Se



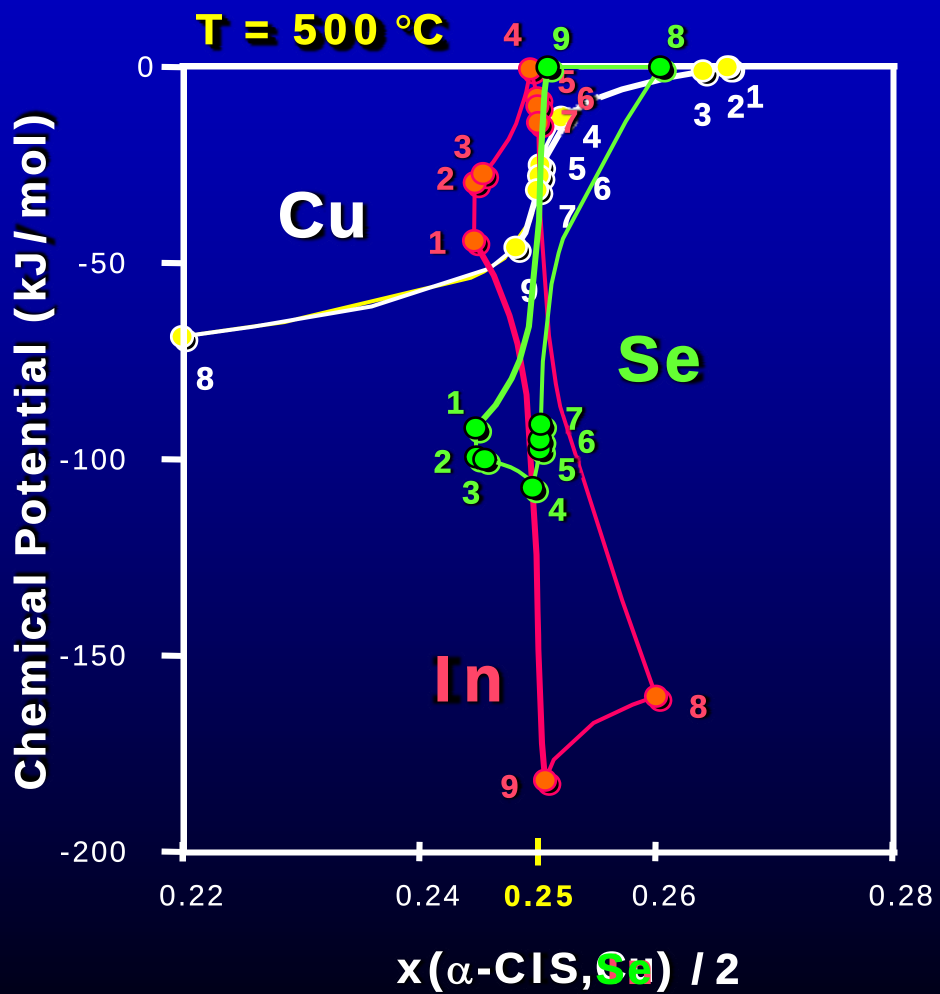
Phase Diagram of Cu-In-Se

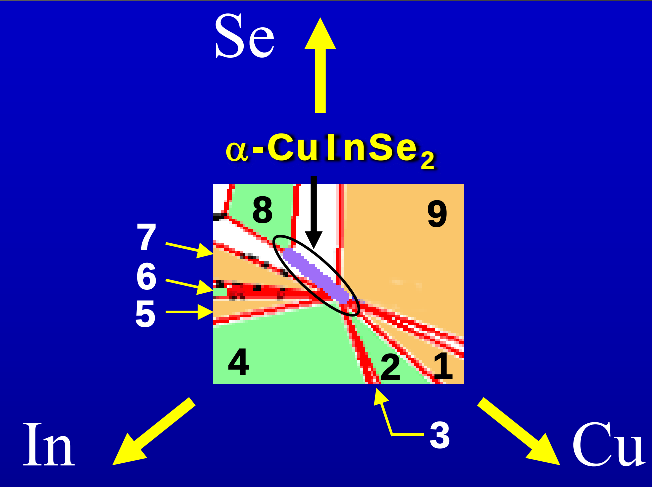
Isothermal section at 500 °C (18 phases)



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

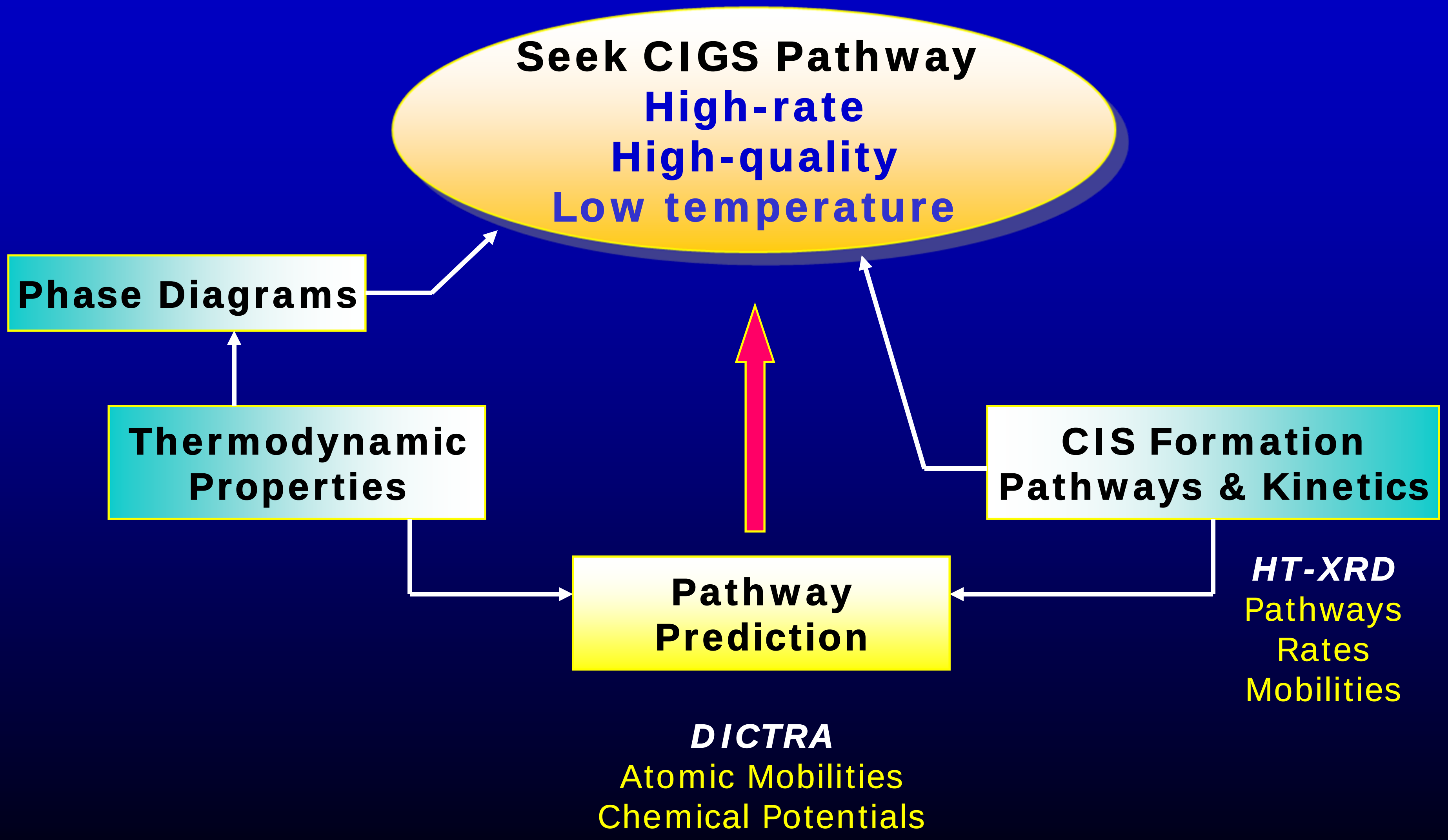
Chemical Potential Diagram





Reg.	Equilibrium phases
1	α-CISe$_2$ + α-Cu + β-Cu$_2$Se
2	α-CISe$_2$ + α-Cu + Cu$_7$In$_3$
3	α-CISe$_2$ + Cu$_2$In + Cu$_7$In$_3$
4	α-CISe$_2$ + Cu$_2$In + In$_4$Se$_3$
5	α-CISe$_2$ + InSe + In$_4$Se$_3$
6	α-CISe$_2$ + InSe + δ-CuInSe$_2$
7	α-CISe$_2$ + β-CuIn$_3$Se$_5$ + δ-CuInSe$_2$
8	α-CISe$_2$ + β-CuIn$_3$Se$_5$ + Liquid
9	α-CISe$_2$ + β-Cu$_2$Se + Liquid

Approach



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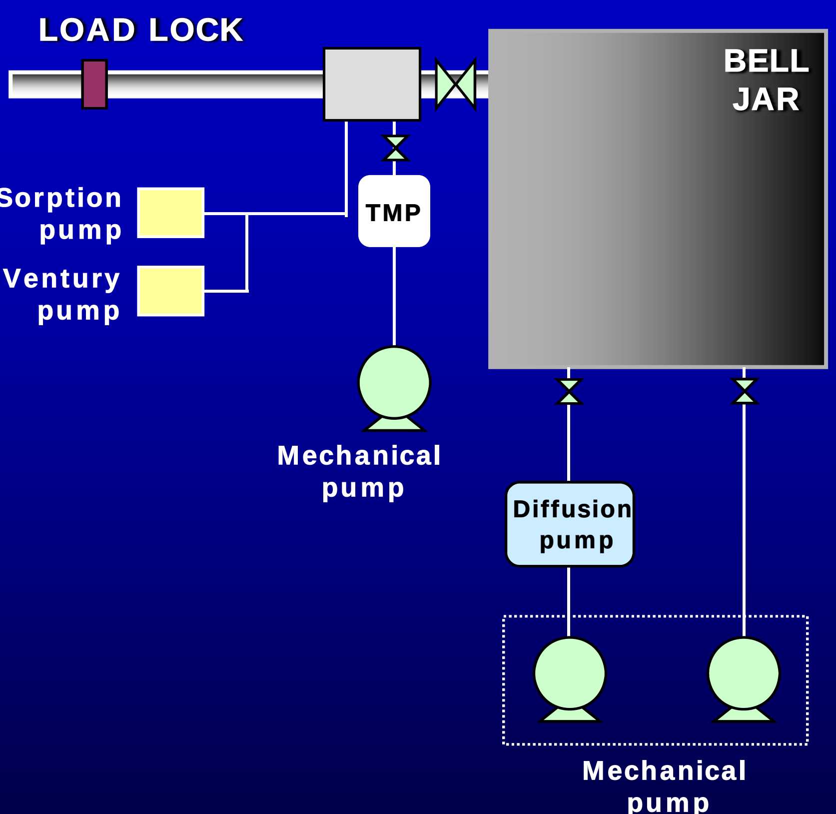
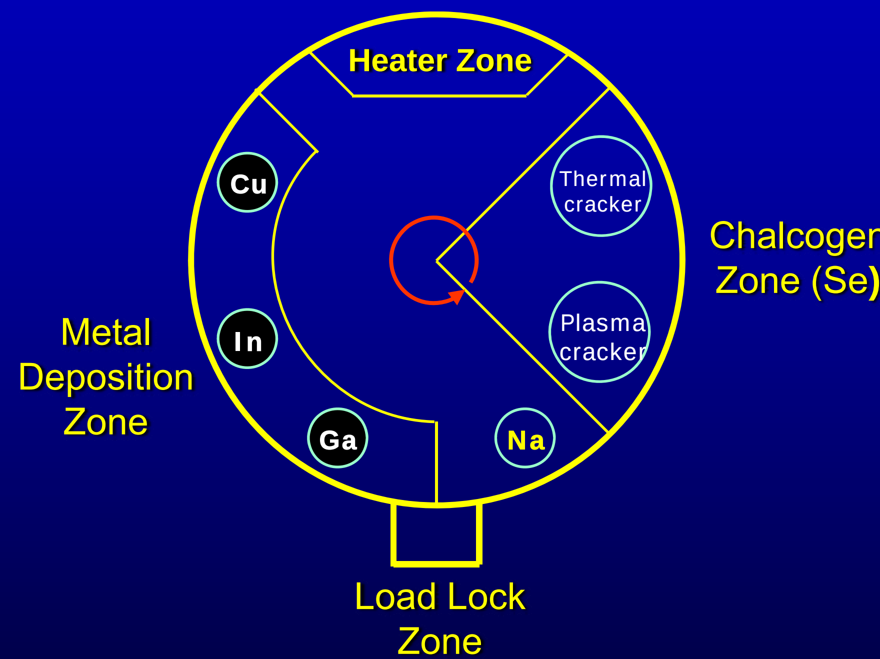
UF PMEE Reactor System



Schematic top view of MEE reactor

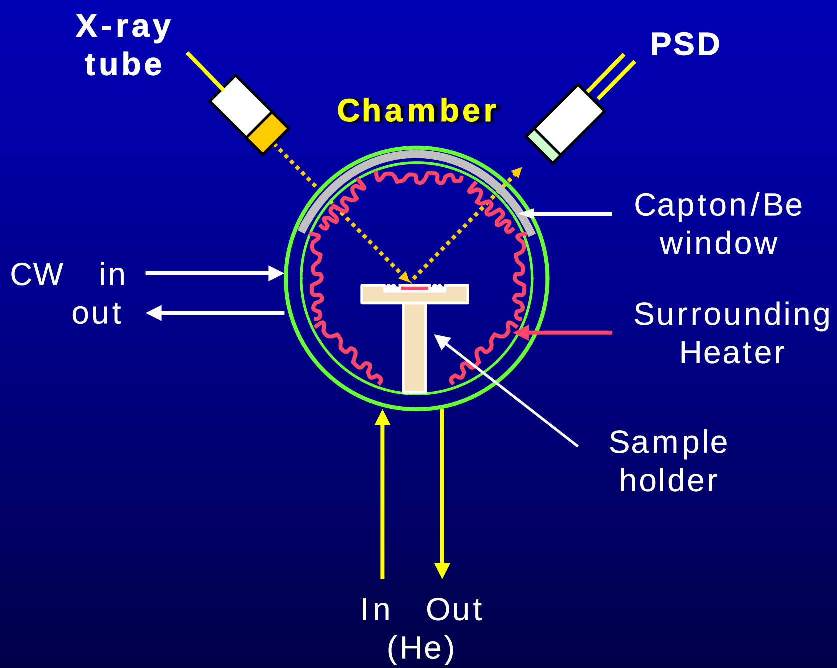


- ➔ Ultra high vacuum system
- ➔ Operating pressure : ~ 10^{-8} Torr

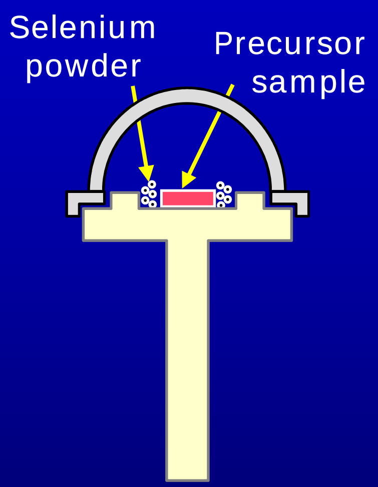
- ➔ Rotating platen with 9 substrates (2×2 inches)
- ➔ Sequential deposition

HT-XRD System

Panalytical Philips X'pert System



Graphite Dome

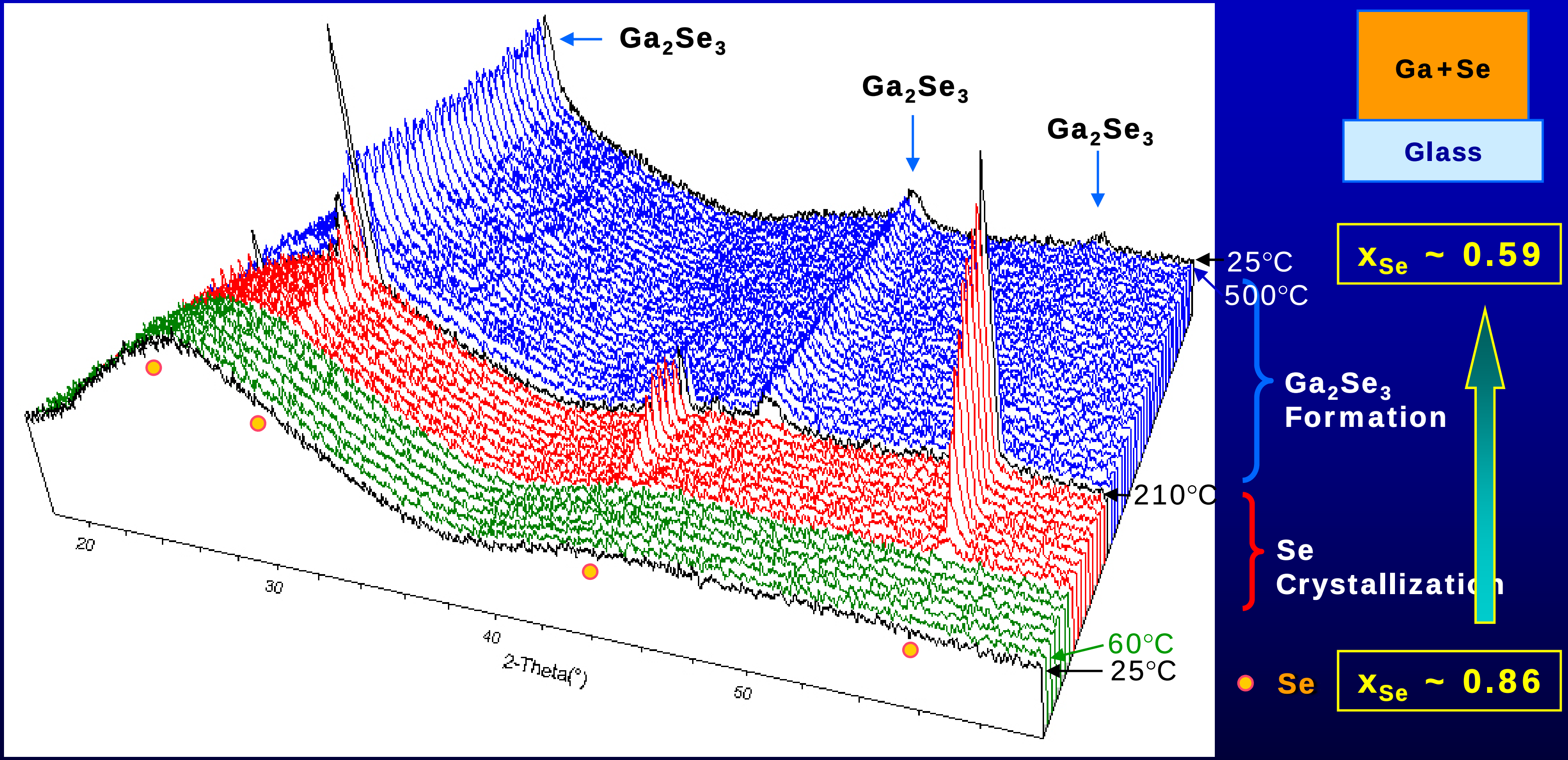


➔ **High Temperature Materials Laboratory (ORNL)**

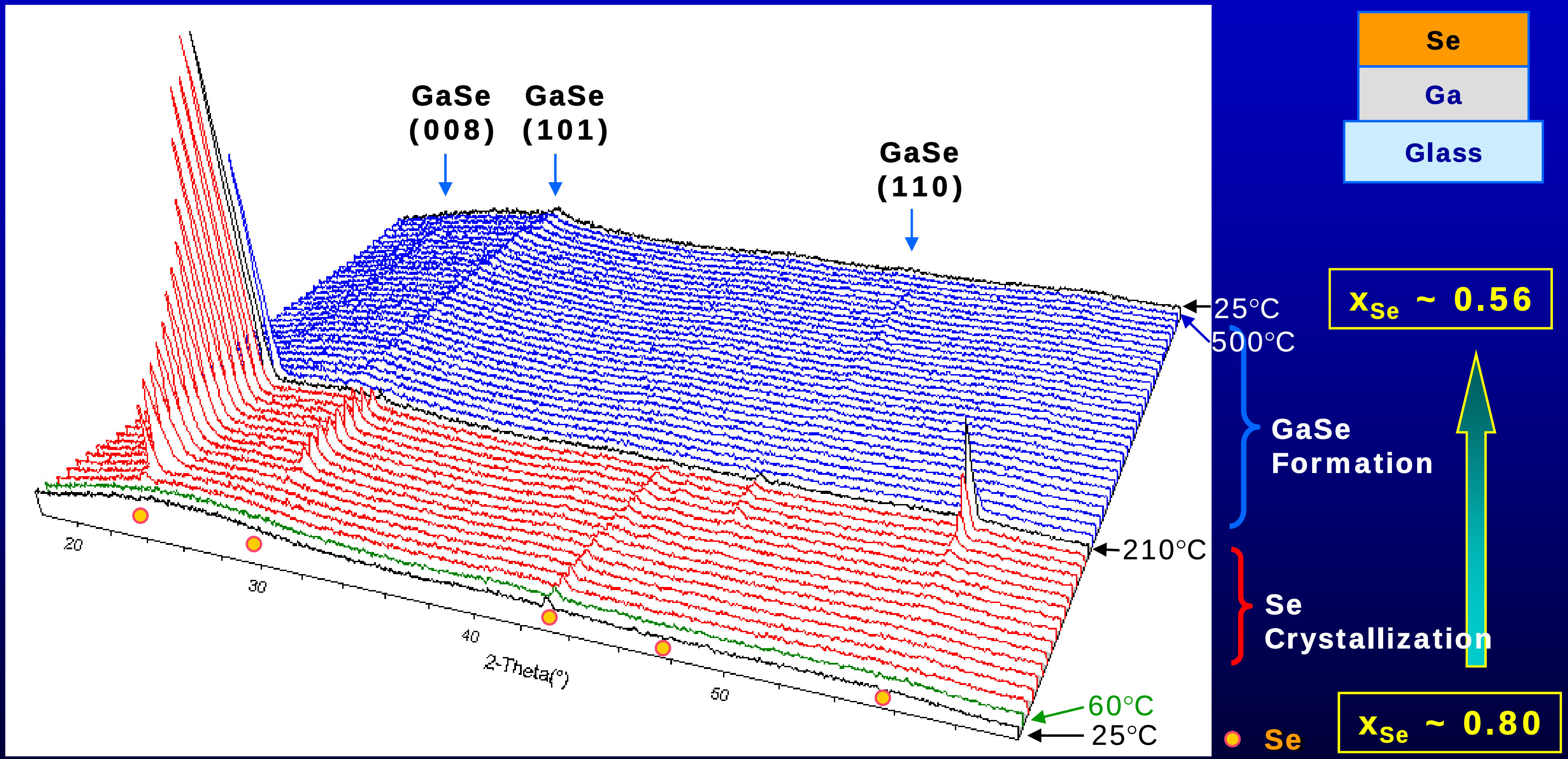
Pathway Studies

- Binary Metal-Se Precursors
  - Co-deposited – Se-M/glass
  - Bilayer – Se/M/glass
- Ternary Precursors
  - Metal Selenization
  - Co-deposited
  - Bilayer Compounds: e.g. CuSe/GaSe/glass
- Quaternary Precursors
- Nanopowders

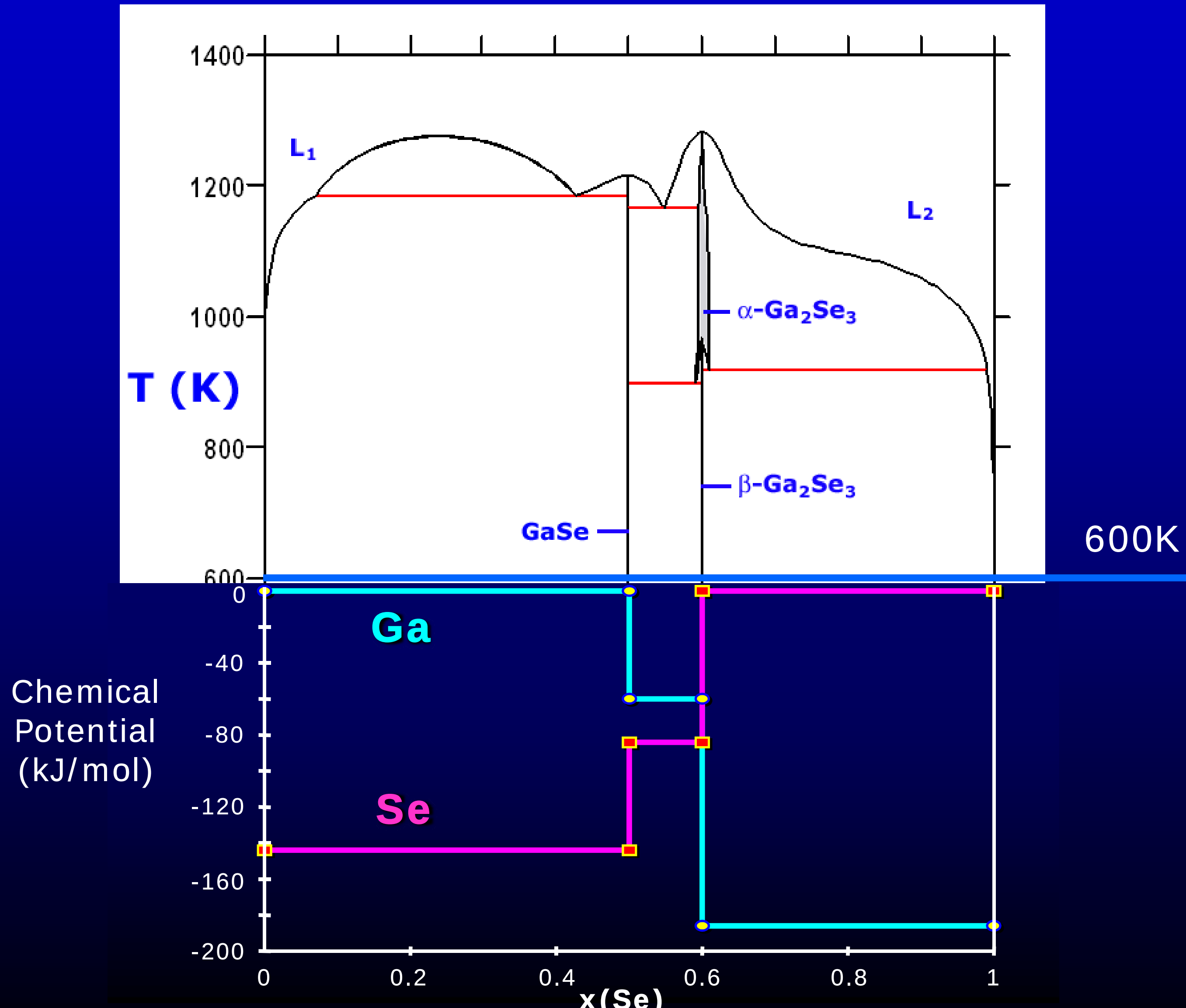
Ga+Se Precursor Annealing



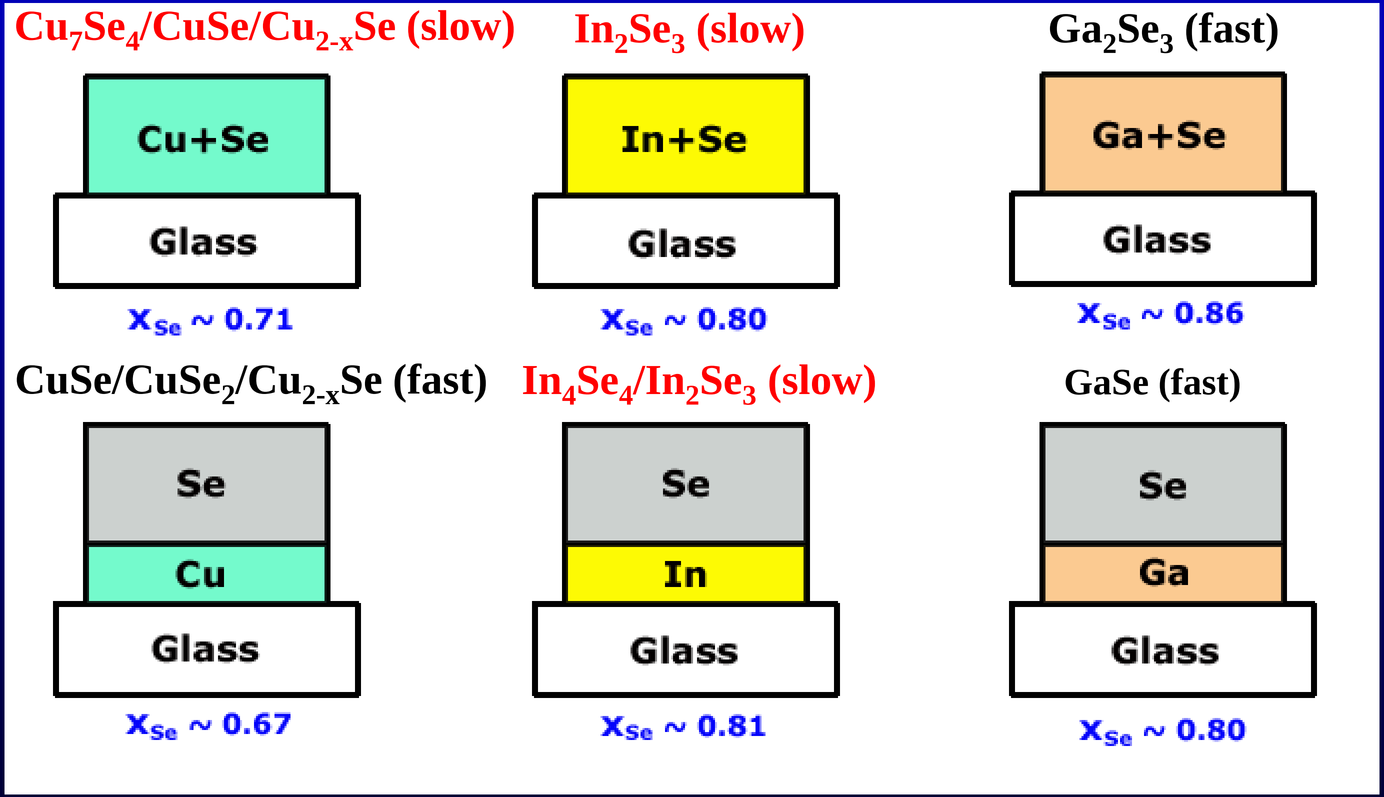
Se/Ga Precursor Annealing



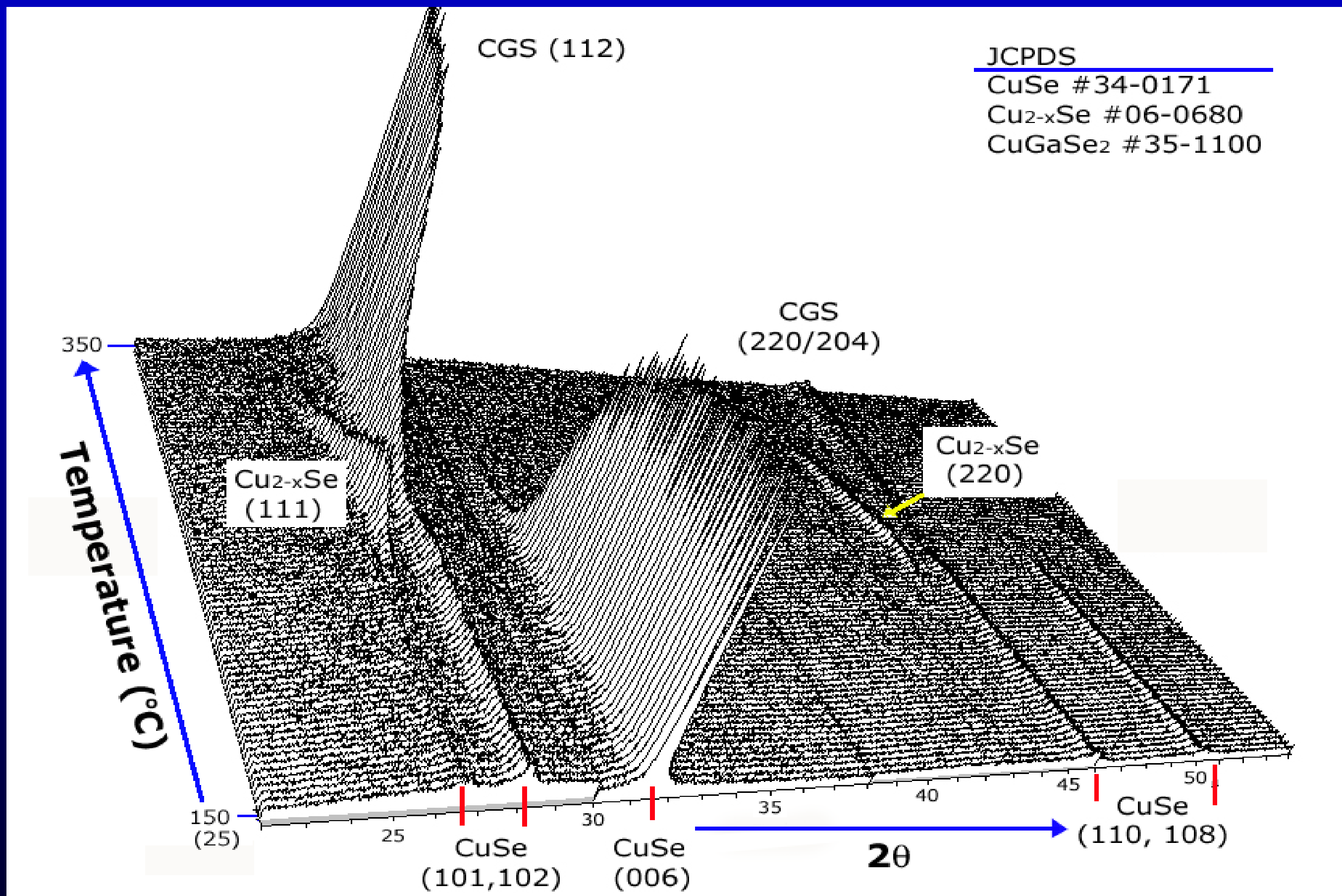
Ga-Se Phase Diagram

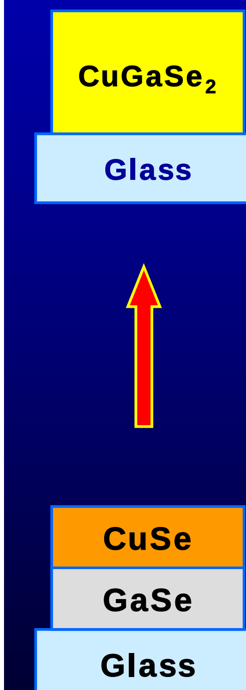


Pathways for Binary Precursor Structures

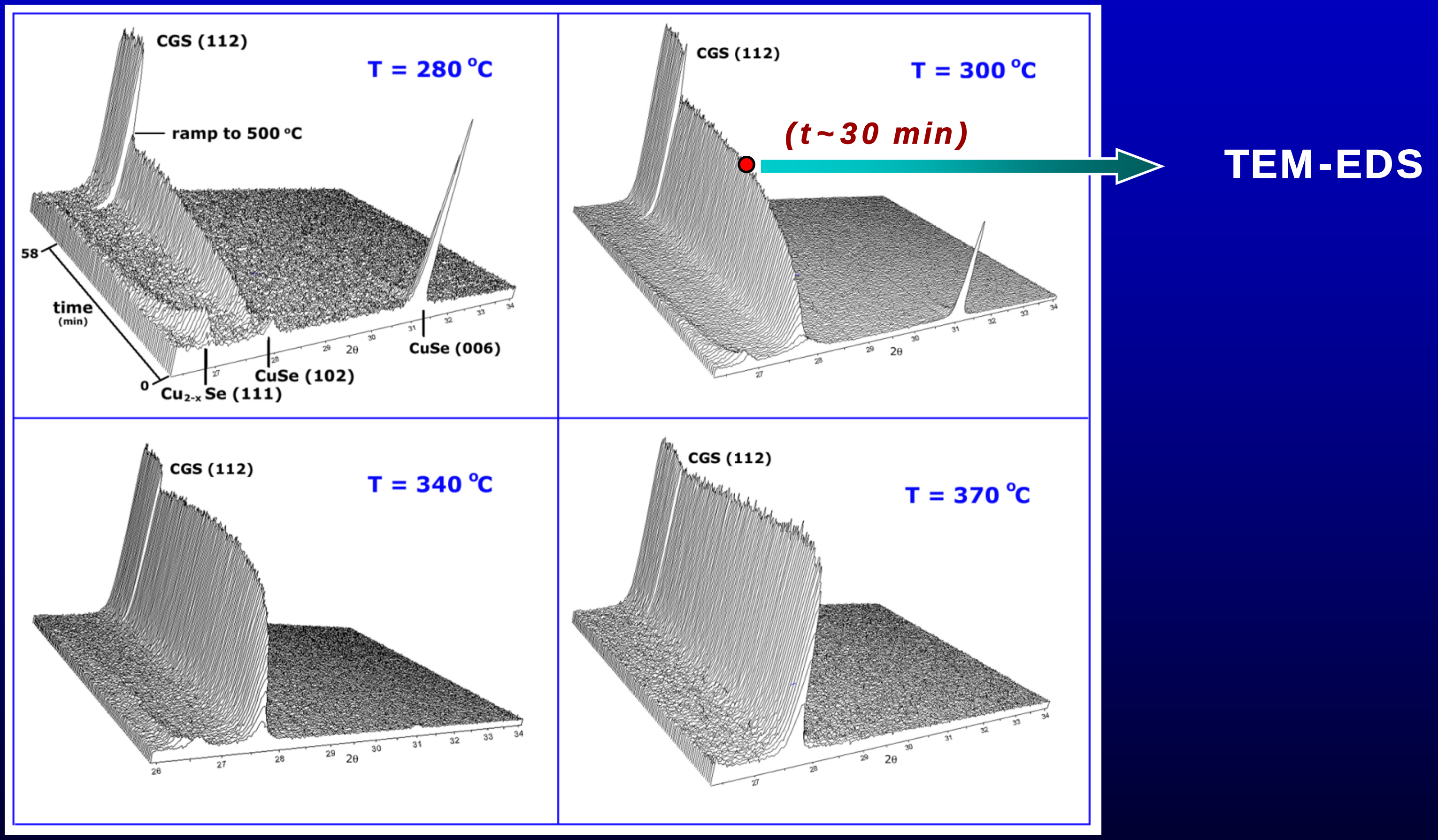


Temperature Ramp Anneal



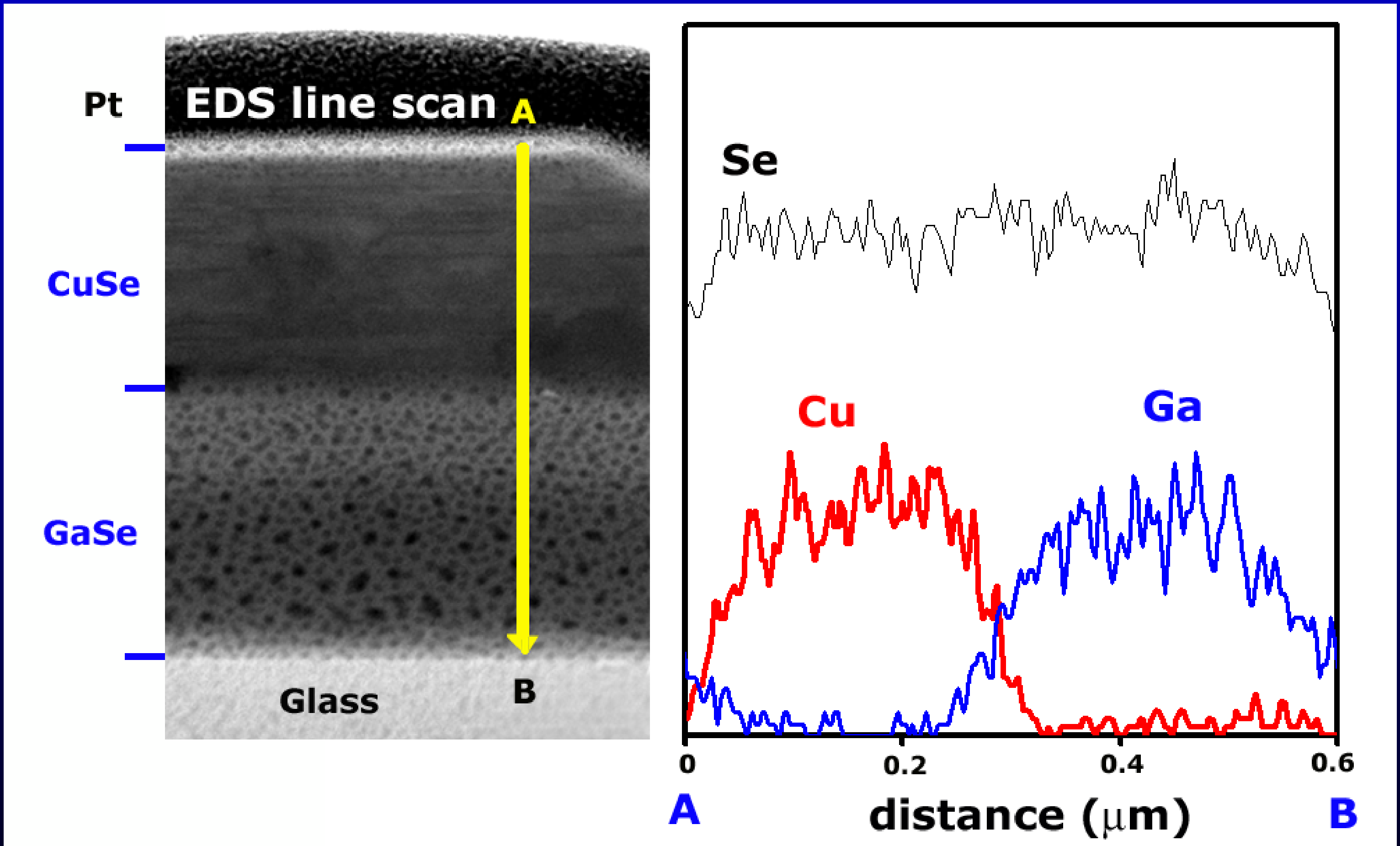


Isothermal annealing



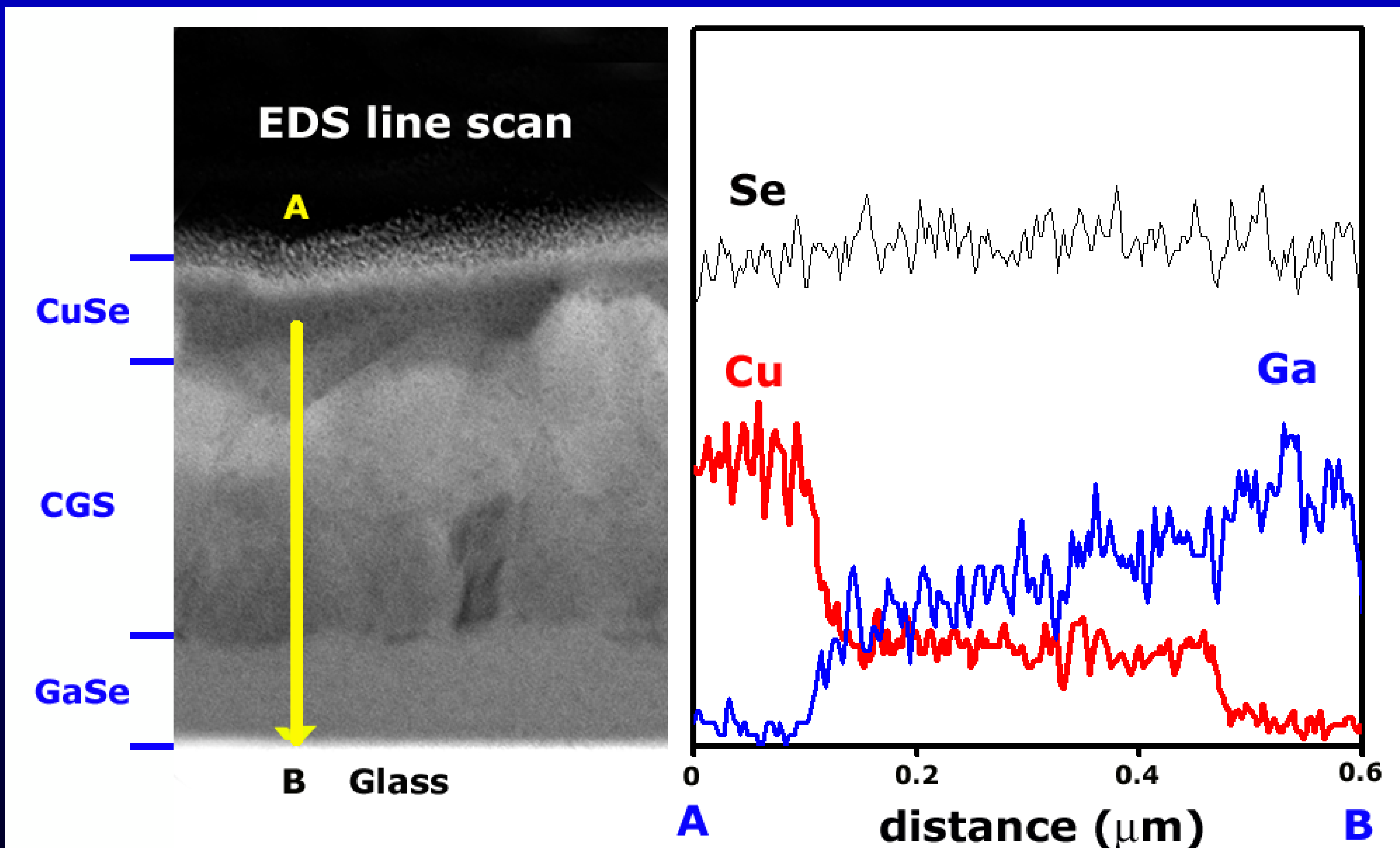
TEM-EDS Analysis

Glass / GaSe / CuSe Precursor

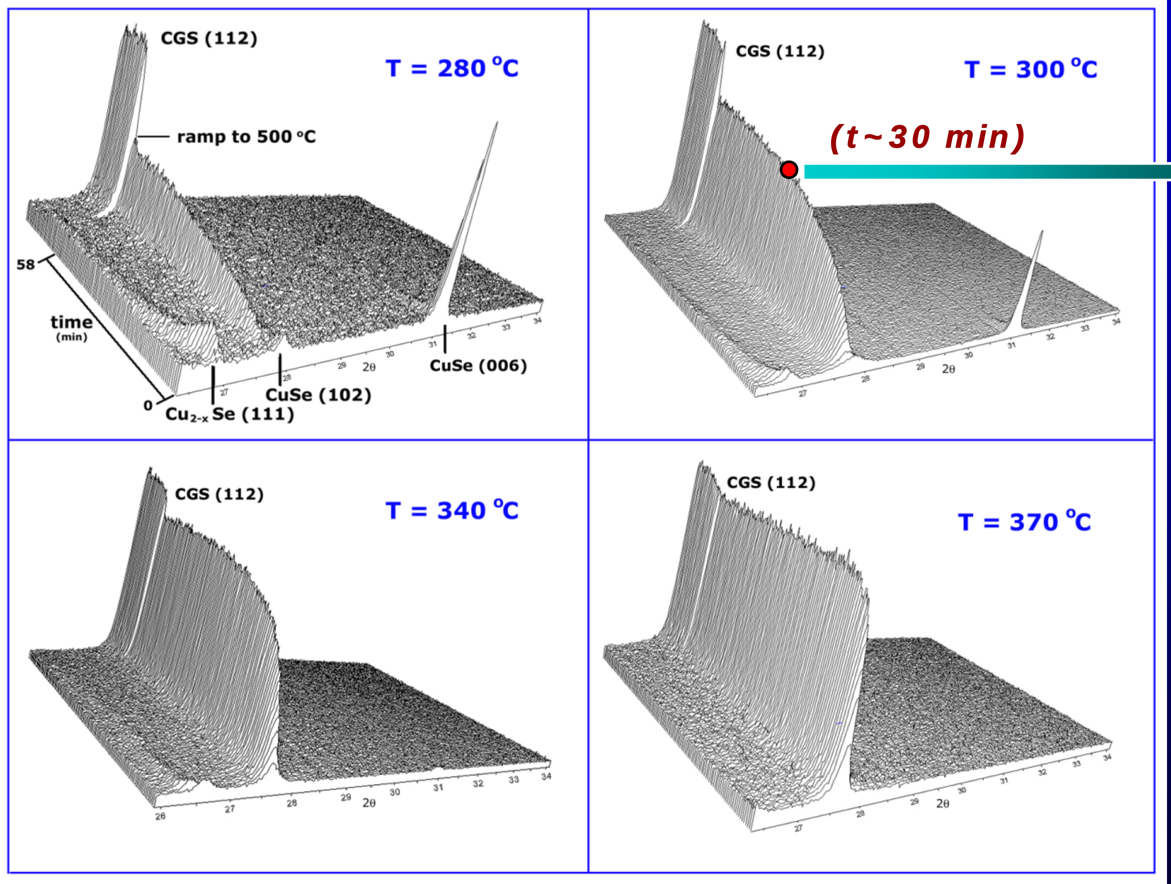


TEM-EDS Analysis

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



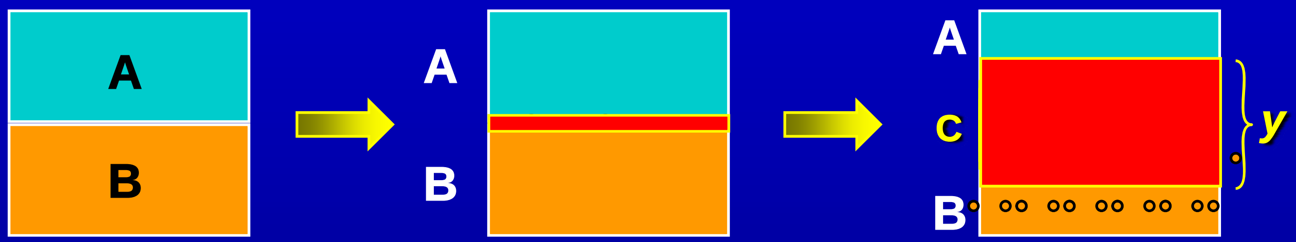
Isothermal annealing



TEM-EDS

Solid-state Growth Models

- **Parabolic growth model**

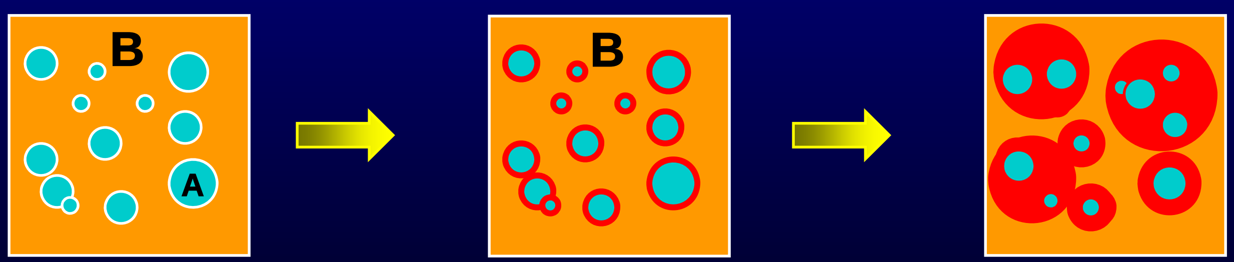


Before reaction | Nucleation at A-B interface | Diffusion thru product & reaction (ex. $D_{BC} > D_{AC}$)

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

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

- **Avrami growth model**



Phase A in matrix B | Nucleation | Diffusion & growth

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

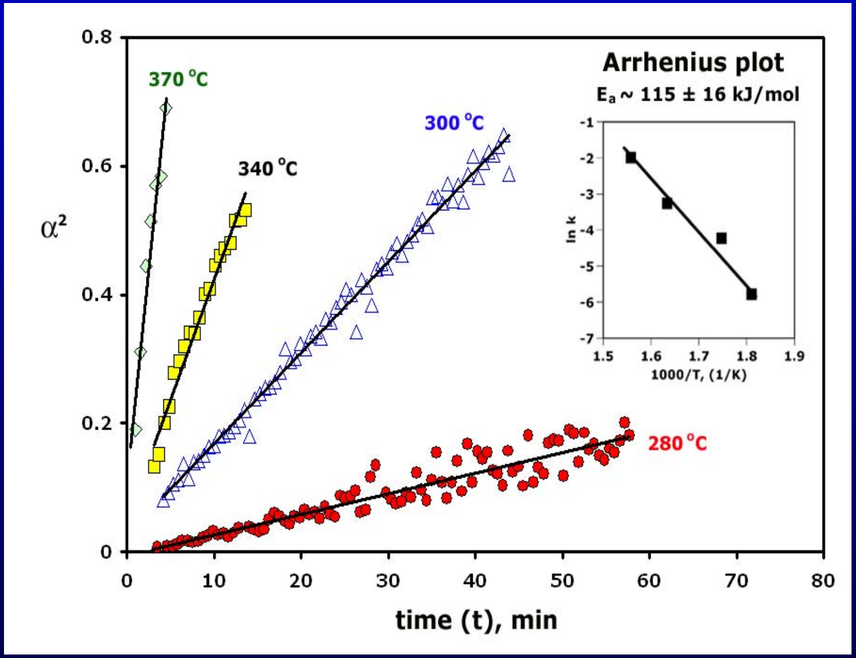
$$\ln[-\ln(1-x)] = n\ln t + n\ln k$$

$$0.5 < n < 1.5$$

(1-D diffusion)

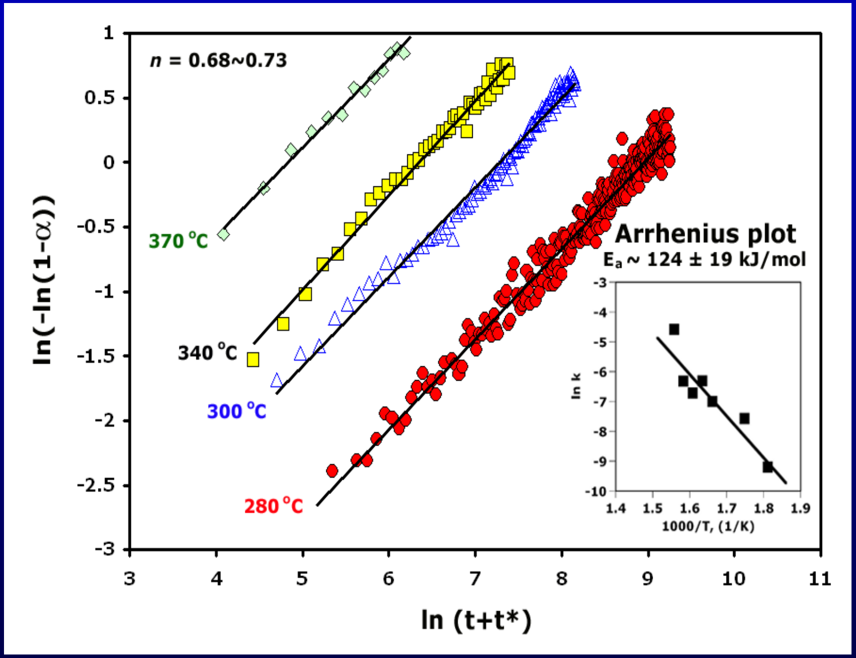
Kinetic Analysis

Parabolic model



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

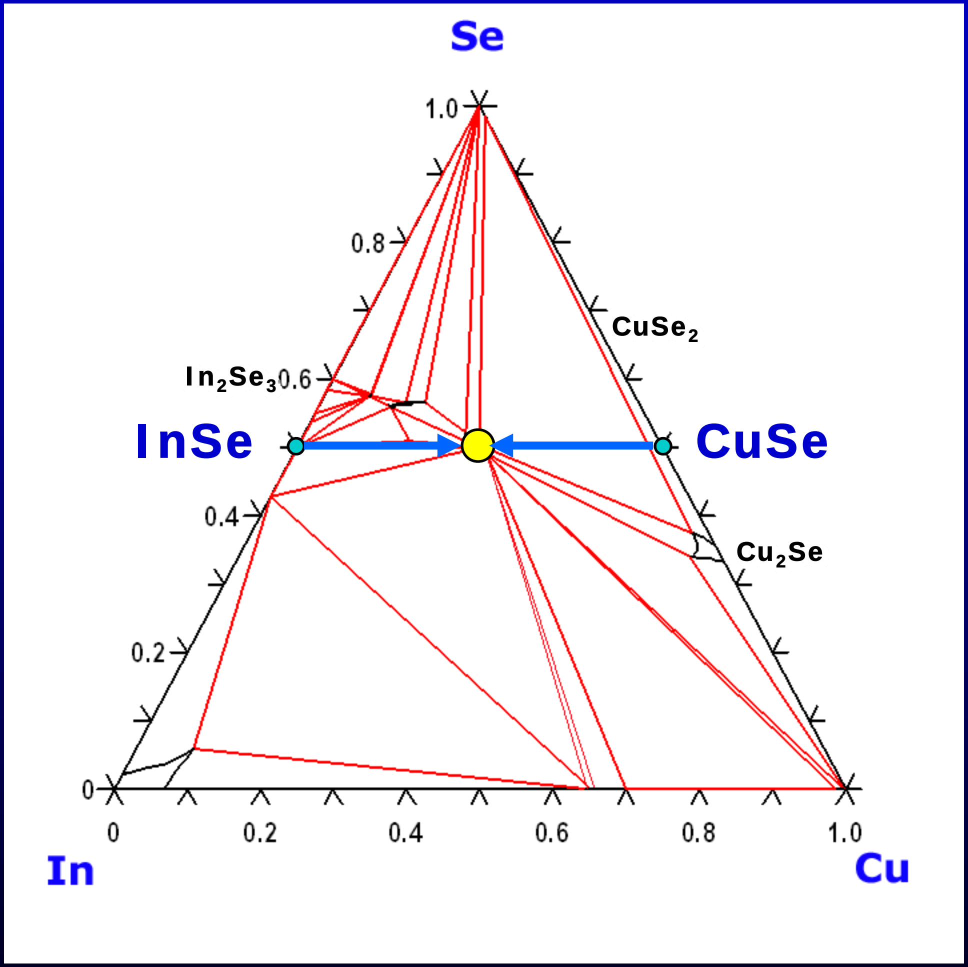
Avrami model

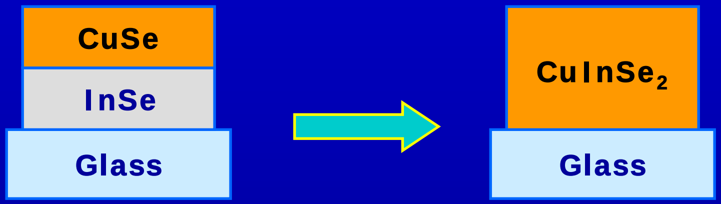


$\ln[-\ln(1-\alpha)] = n\ln(t+t^*) + n\ln k$

➔ Analysis suggests one-dimensional diffusion controlled reaction

$CuInSe_2$ Formation Pathway

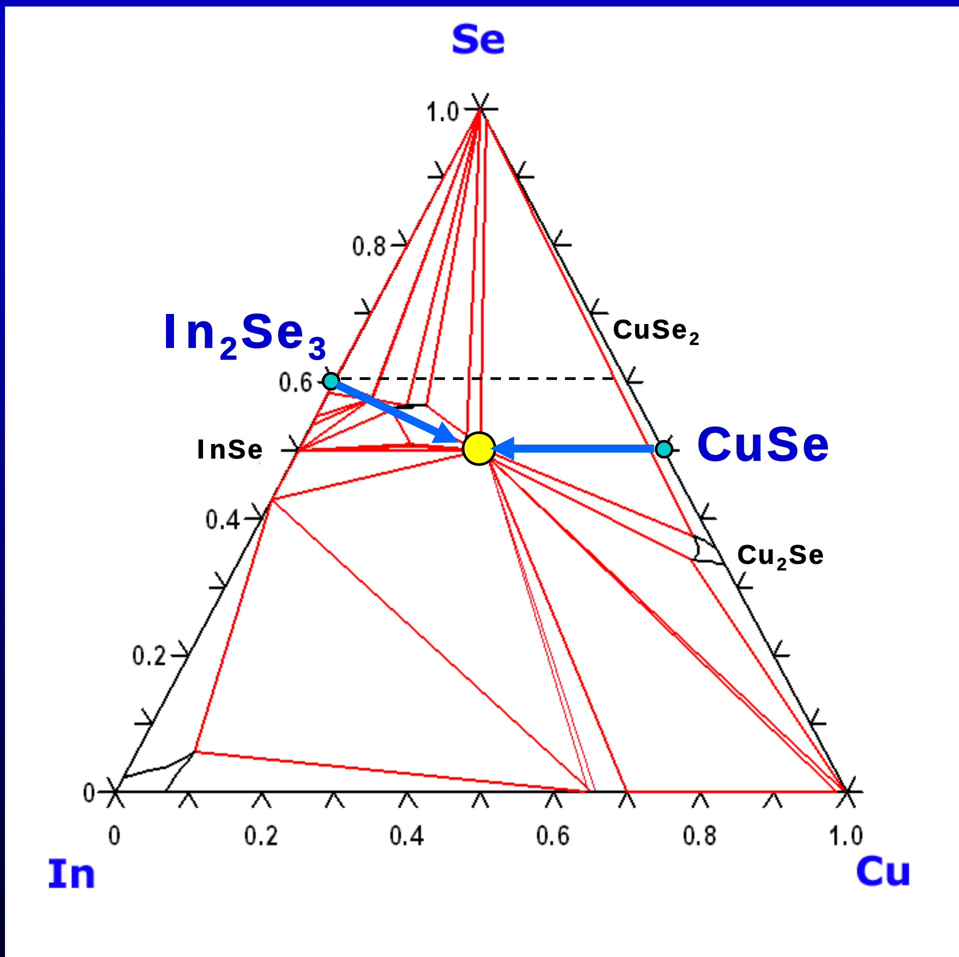


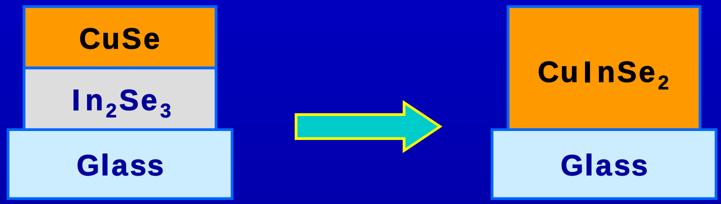


$CuSe + InSe \rightarrow CuInSe_2$

$(E_a = 66\ kJ/mol)$

$CuInSe_2$ Formation Pathway

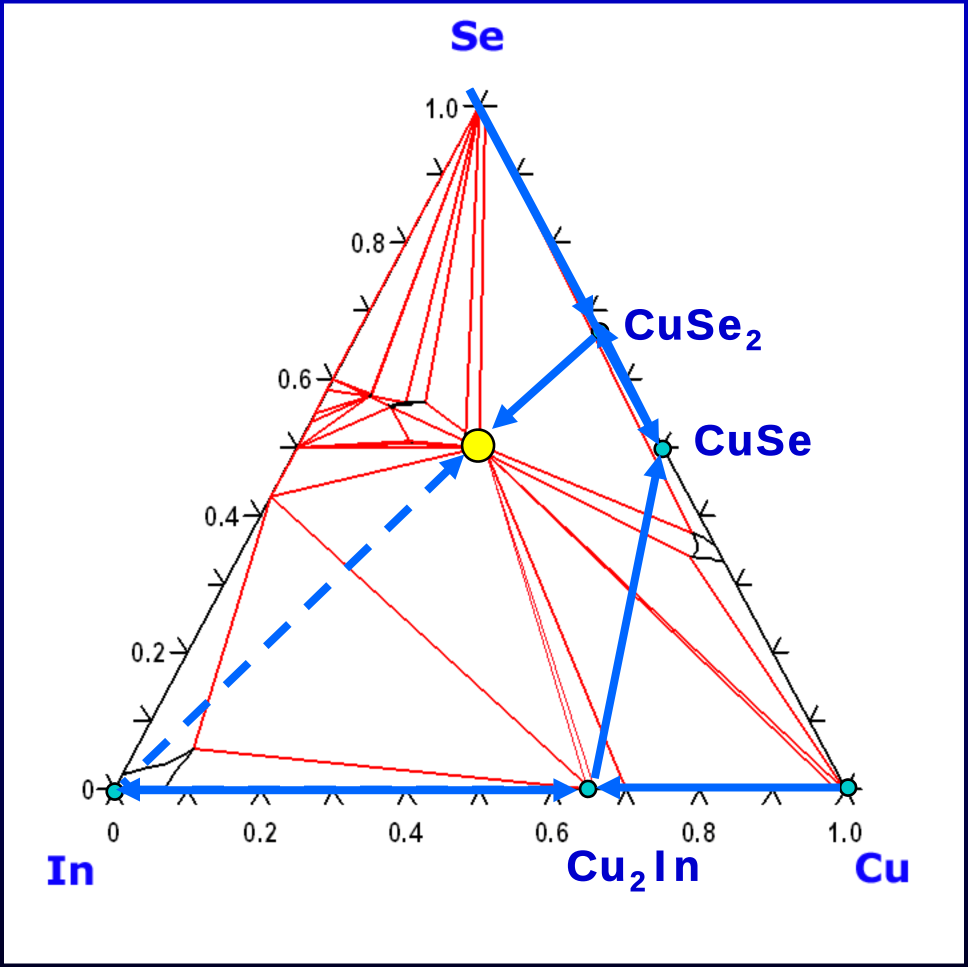




$$CuSe + In_2Se_3 \rightarrow CuInSe_2 + Se$$

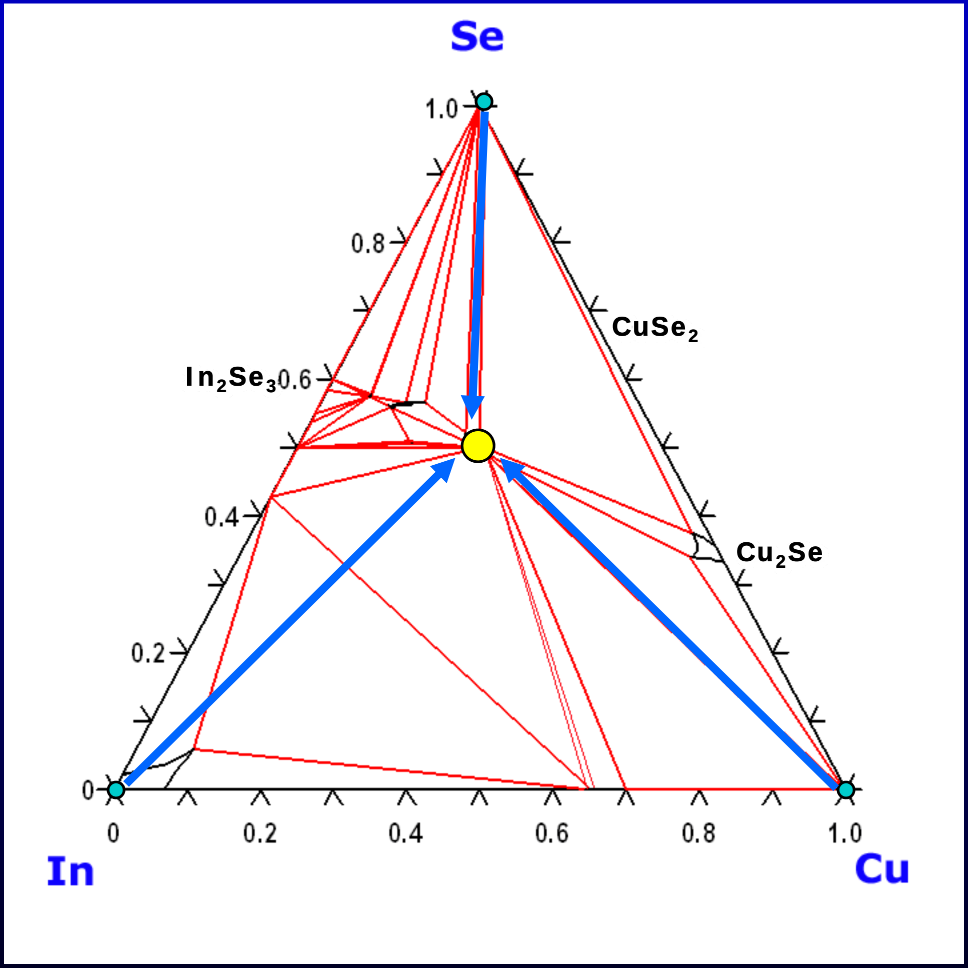
$$(E_a = 162\ kJ/mol)$$

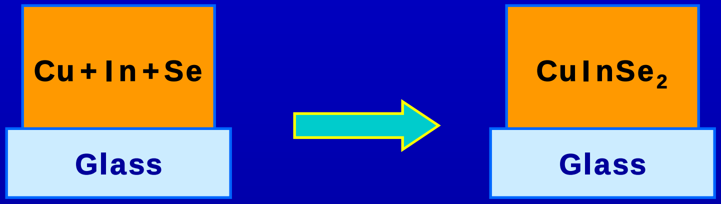
$CuInSe_2$ Formation Pathway



(E_a=100 ~ 124 kJ/mol)

$CuInSe_2$ Formation Pathway





$Cu + In + Se \rightarrow CuInSe_2$

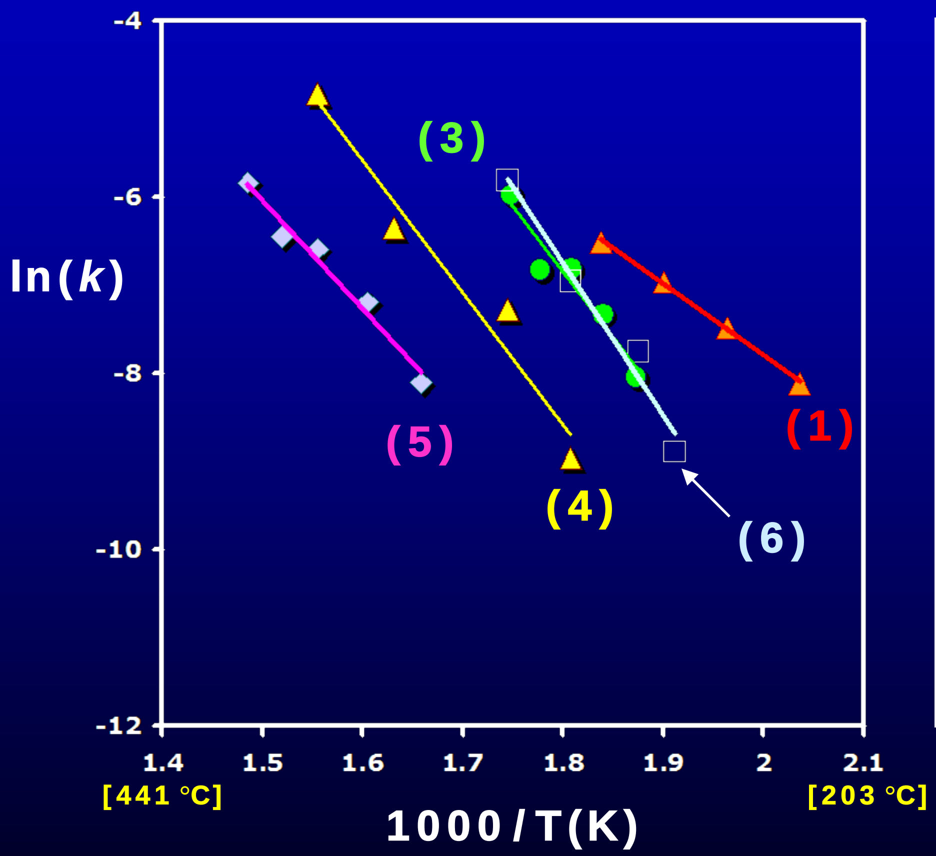
Very fast !!

No intermediate phase

No diffusion barrier !!

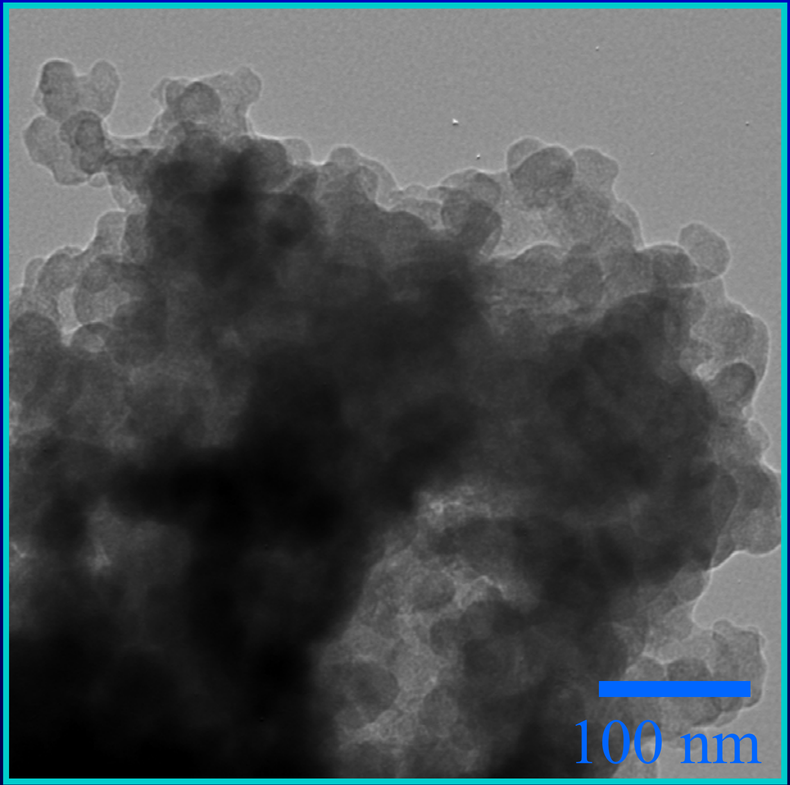
Reaction rate

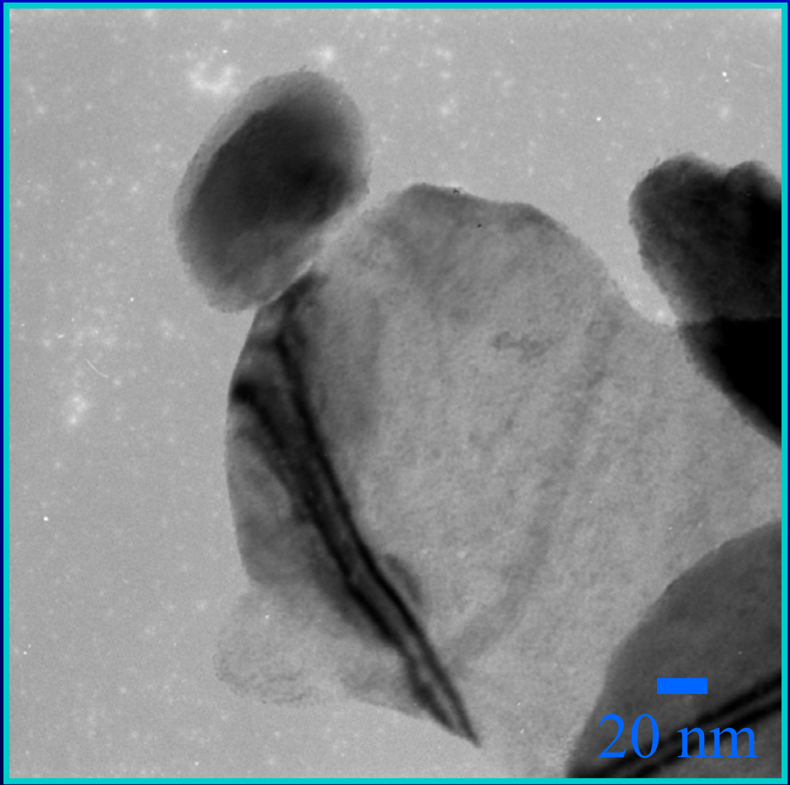
- **Avrami model**



	Precursors	Activation energy (kJ/mol)	
		Avrami	Parabolic
1	InSe/CuSe	**66**	65
2	$CuSe/In_2Se_3$	N/A	162 (±5)
3	Cu-In + Se(vapor)	**124 (±19)**	100 (±14)
4	GaSe/CuSe	**118 (±22)**	107 (±15)
5	Cu-Ga + Se(vapor)	**108**	N/A
6	Cu/In/Ga + Se(vapor)	**144**	N/A

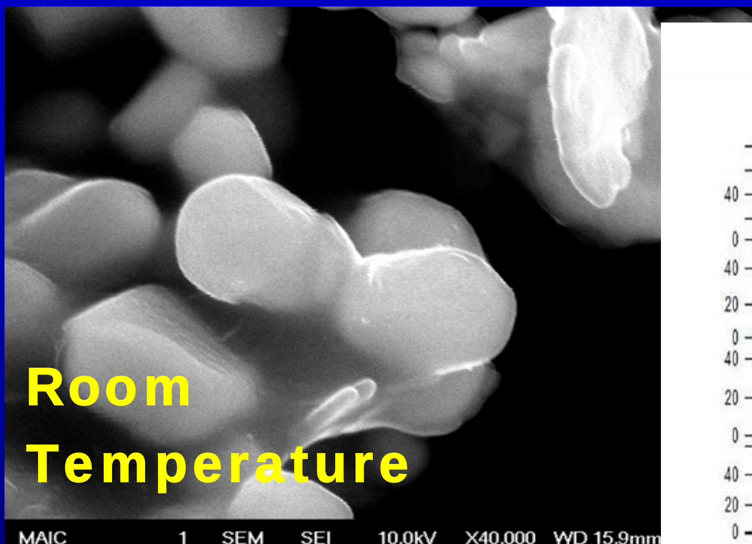
TEM Image: CIS Nano-particles

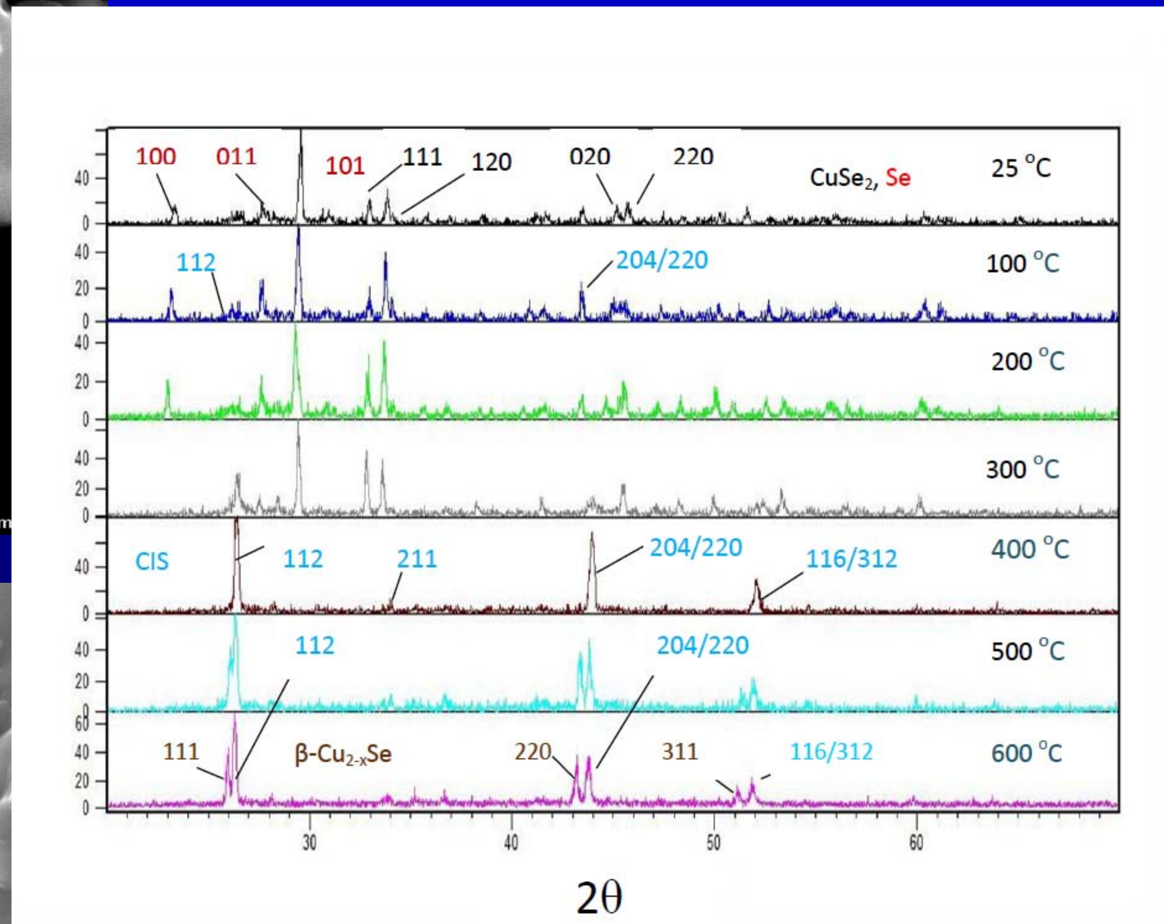


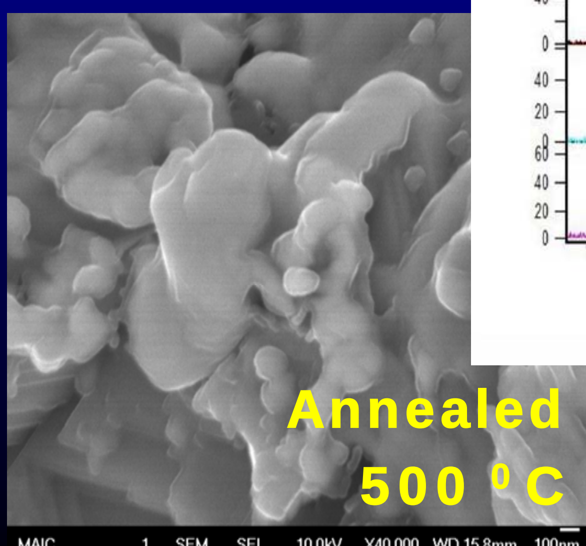


U. Farva & C. Park

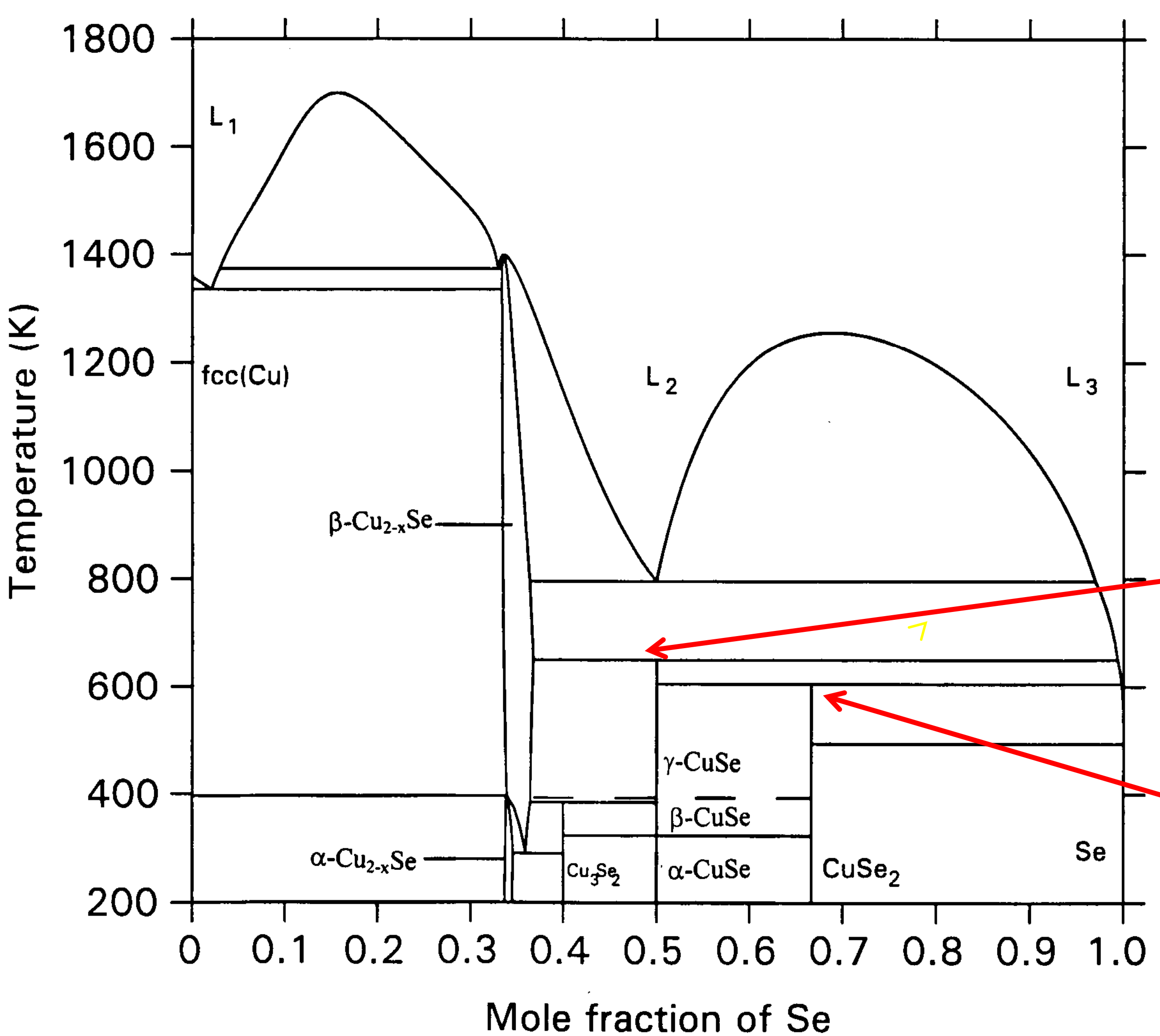
HT-XRD Cu-rich CIS Nanoparticles
As-deposited: CIS, $CuSe_2$ and Se







Cu-Se Phase Diagram



β-$Cu_{2-x}Se + L_3 \leftrightarrow \gamma$-$CuSe$
652.7K (379.5 °C)

γ-$CuSe + L_3 \leftrightarrow CuSe_2$
605K (331.8 °C)

How Can We Synthesize High Quality CIGS Rapidly?

Sutton's law states that in attempting to diagnose a problem, one should first do the experiment that can confirm the most likely diagnosis. "When you hear hoof beats in Texas, think horses, not zebras."

Conclusions

- **Pathways are dependent on precursor structure**
  - In phase particularly important
- **Most paths are diffusion limited**
- **High-rate processes are possible**
  - Film quality needs assessed
  - Liquid phase assisted growth
- **Point defect chemistry helpful (low disordering energy)**
  - Enhance diffusivity, defect compensation, type-inversion, impurity passivation