Notes on Diffusion Data in the Cu-In-Se System for Application in CIS photovoltaic cells

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Binaries in the Cu-In-Se System

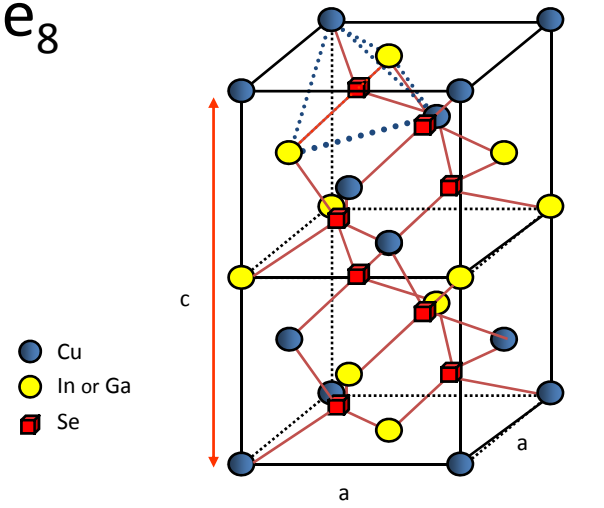
- Cu-In binary system
  - 3 solution phases: liqud, fcc(Cu) and β (bcc)
  - 2 ordered phases: γ and η´
  - 3 stoichiometric phases: δ (Cu0.7In0.3), η (Cu0.64In0.36) and $Cu_{11}In_9$
- In-Se
  - 2 solution phases (Se and In)
  - 1 ionic liquid
  - 6 stoichiometric phases (In_4Se_3, InSe, In_6Se_7, In9Se11, In5Se7 and the polymorphic In_2Se_3 (α,β,γ,and δ)
- Cu-Se
  - -2 solution phases fcc(Cu) and Se
  - 1ionic liquid
  - 3 stoichiometric compounds: $Cu_{2-x}Se$, Cu_3Se_2,CuSe and $CuSe_2$
    - $Cu_{2-x}Se$ has 2 polymorphs (α and β)
    - CuSe has 3 polmorphs α-CuSe, β-CuSe and γ-CuSe
  - 1 ordered phase $Cu_{2-x}Se$ which has 2 polymorphs (α and β)
    - 3 sublattice model (Cu,Va)1(Se)1(Cu)1

Thermodynamics from W.K. Kim and J. Y. Shen and T. Anderson

Ternary Cu-In-Se

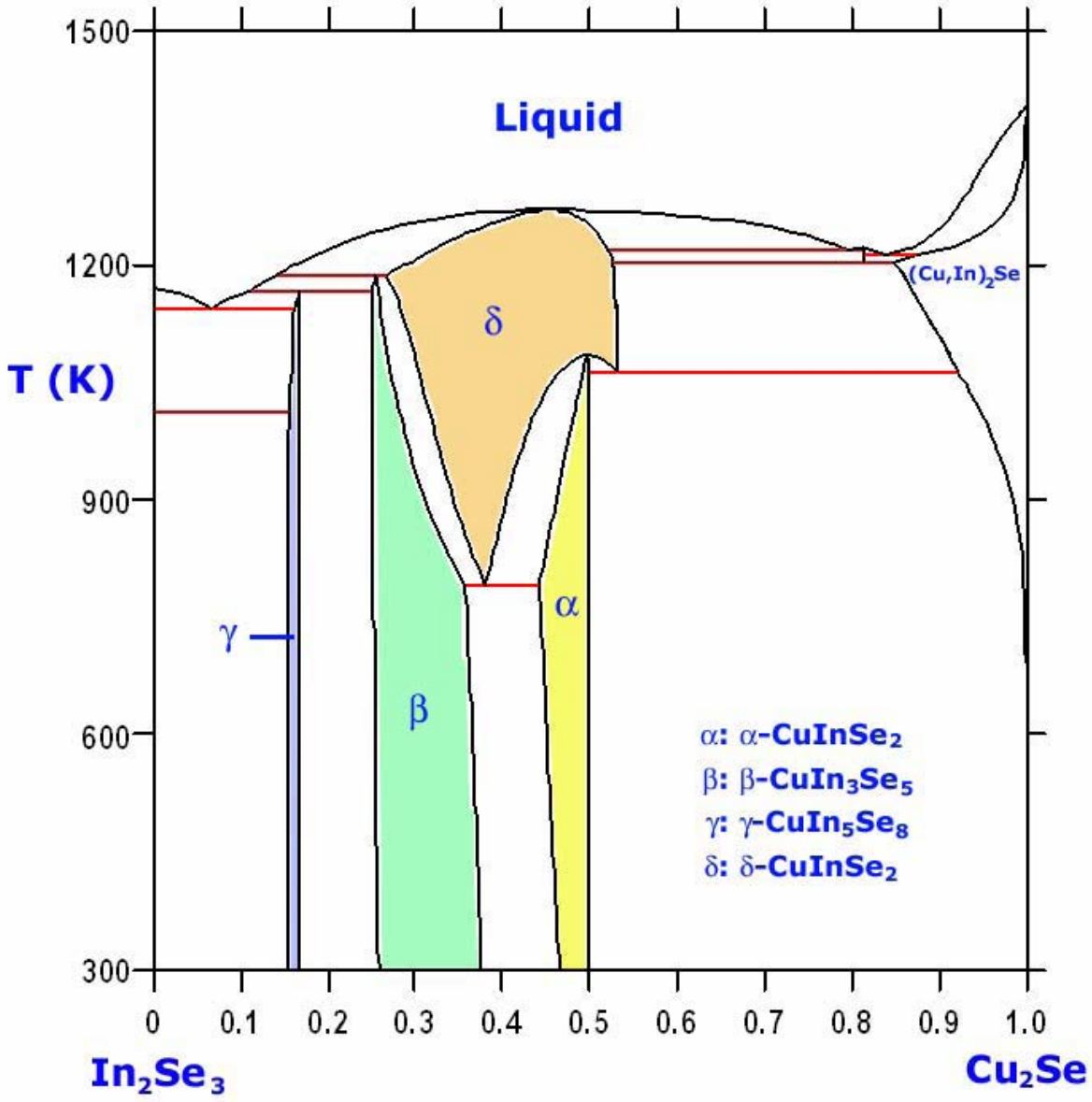
- 1 Ionic Liquid (Cu+1, In+3) (Se-2, Va, Se)
- α $CuInSe_2$ (Cu%,In,Va)(Cu,In%,Va)Se_2 (Chacopyrite)
- δ $CuInSe_2$ $(Cu\%,In,Va)_2$ Se $(Se,Va)_2$ (Sphalerite)
- β $CuIn_3Se_5$ (Cu%,In,Va) $(Cu,In,Va)_3Se_5$ (Defect Chacopyrite)
- γ $CuIn_5Se_8$ (Cu%,In,Va) $(Cu,In\%,Va)_5$ Se_8
- Cu_2In $(Cu,In)_2(Cu,In)(Se,Va)$
- β Cu_2Se (Cu,Va) Se (Cu,In)

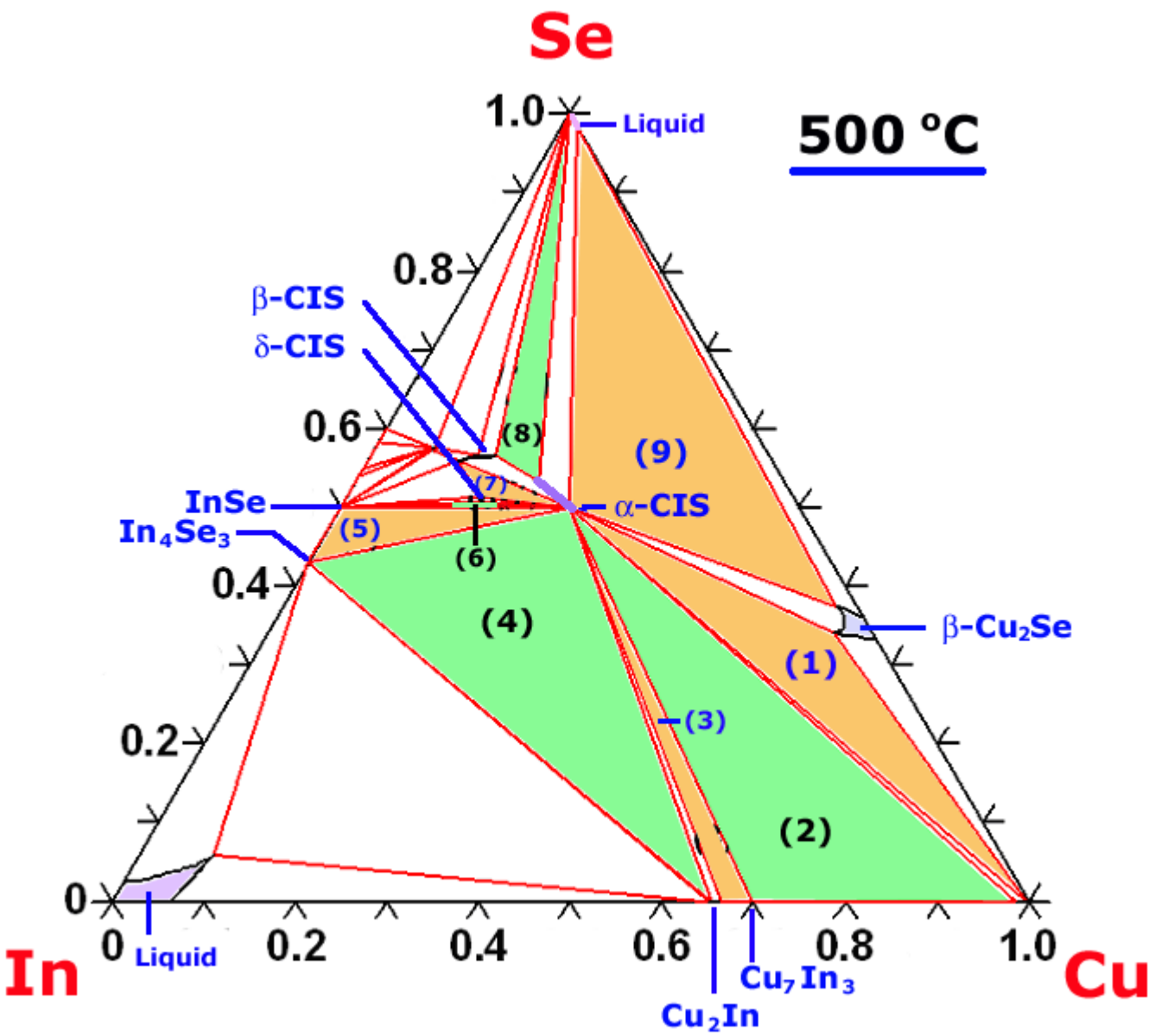
Assume α–$CuInSe_2$ is composed of a cubic cation sublattice and a cubic anion sublattice.



Chalcopyrite CIGS structure

Thermodynamics from W.K. Kim and J. Y. Shen and T. Anderson


1500
1200
900
600
300
T (K)
Liquid
δ
γ
β
α
(Cu,In)2Se
α: α-CuInSe2
β: β-CuIn3Se5
γ: γ-CuIn5Se8
δ: δ-CuInSe2
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
In2Se3
Cu2Se


Se
500 °C
Liquid
β-CIS
δ-CIS
InSe
In4Se3
α-CIS
β-Cu2Se
(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
(9)
1.0
0.8
0.6
0.4
0.2
0
In
Cu
Liquid
Cu7In3
Cu2In

Processing of α-CuInSe

- Co-Deposition of elements
- Annealing of stacked elemental layers
- Direct compound formation
- Selenization of metal particles

Reactions during Thermal Processing

- $CuSe+InSe \rightarrow CuInSe_2$
- $Cu_2Se+2InSe+Se \rightarrow 2CuInSe_2$
- $Cu_2Se+In_2Se_3 \rightarrow 2CuInSe_2$

(Herget et. al. J. Phys. Chem. Solids 66 (2005) 1903-1907.) Precursors $Cu_{11}In_9$ $CuIn_2$ $CuSe_2$ In_4Se_3 stacked elemental layers

Kim et al. J.Phys. Chem Solids. 66 (2005) 1915-1919:

α-$CuInSe_2$ form from an In_2Se_3/CuSe bilayer precursor film.

Matsushita et al. J. Cryst. Growth 237-239 (2002) 1986-1992.

Chemical reactions occurring to synthesize a single phase

Cu+In+2In

(1) In, Se → In_2Se, In_6Se_7 at 250C

(2) Cu,Se → Cu_3Se_2, Cu_7Se_4 at 280-420C

(3) In_2Se: solid → liquid at 500C

(4) InSe, In_6Se_7: solid→ liquid at ~ 600 C

(5) In_2Se_3: solid → liquid at ~ 900 C

(6) Cu_7Se_4, InSe, In_2Se_3 → $CuInSe_2$ above 950 C

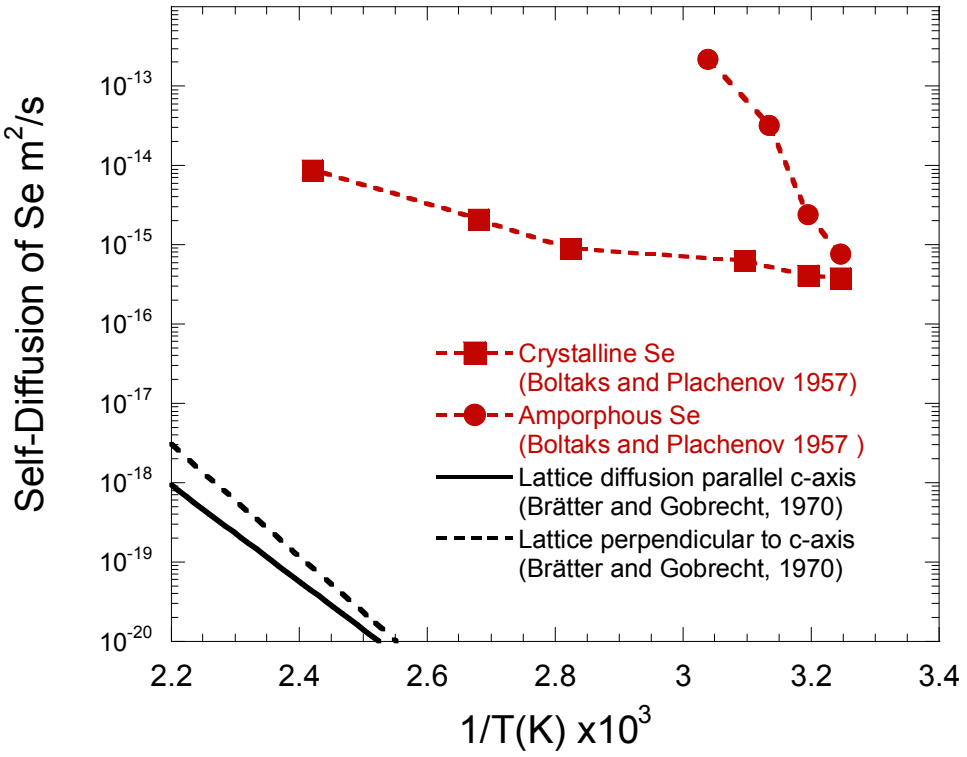
(7) $CuInSe_2$ (spalerite): solid → liquid at 996 C

Reactions during Thermal Processing

- CuIn+2Se
  - $Cu_{1-x}In$ (x>0.5), Se → $CuInSe_2$, InSe at 520C
  - $Cu_{1-x}In$ (x<0.5), Se InSe →$CuInSe_2$ at 575 C
  - InSe: solid → liquid at 650 C
  - $CuInSe_2$: chalcopyrite →spalerite at about 810 C
  - CuSe, InSe → $CuInSe_2$ above 950 C
  - $CuInSe_2$ (spalerite) : solid → liquid at 996 C.
- W. Kim (J. Crystal Growth, 294 (2006) 231-235
  - α-$CuInSe_2$ form by selenization by Cu-In precusor
- Other precusors noted Cu_7In_3 η-$Cu_{16}In_9$ $Cu_{11}In_9$

Se Self-Diffusion

Se Crystal Structure: Trigonal (monoclinic)



First experiments by Boltaks and Plachenov 1957

- Used a hexagonal form of Se
- Performed tracer diffusivities experiments with Se^{75} using sectioning methods

Brätter and Gobrecht (1970) measured lattice diffusion and short circuit diffusion for the self diffusion of Se in single crystals

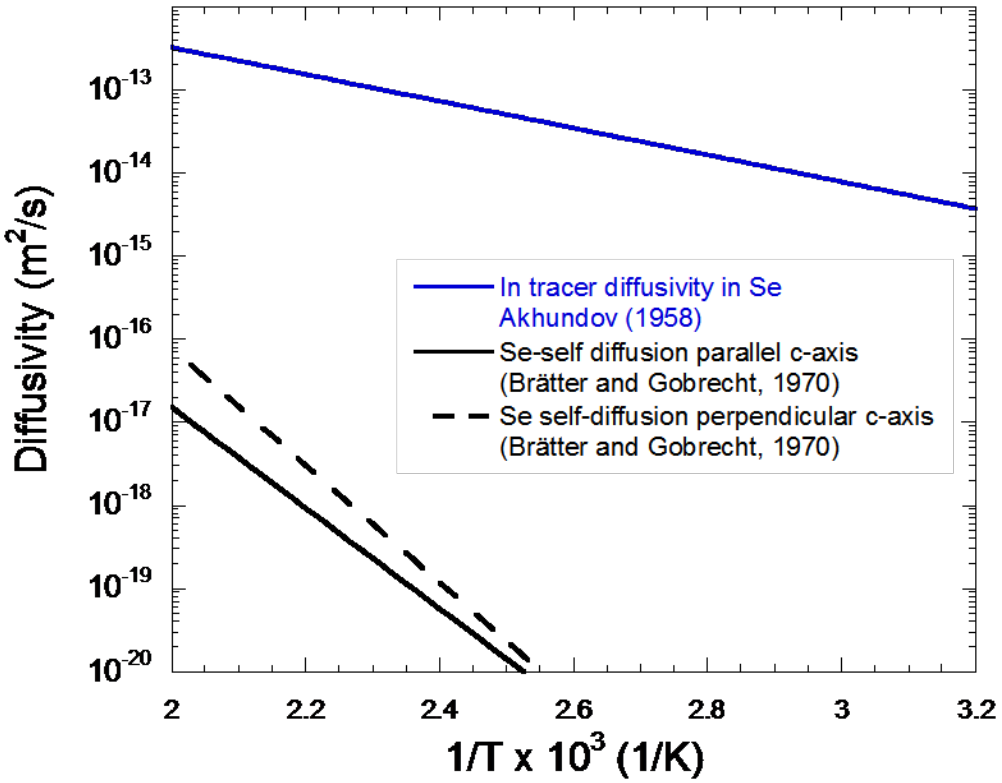
Boltaks and Plachenov most likely measured a short-circuit diffusivity.

B. I.Boltaks and B. T. Plachenov, Zhur. Tekh. Fiz., 27 (1957) 2229.

Brätter and Gobrecht, Self-Diffusion in Se, Phys. Stat. Solidi, 37 (1970) 869-78.

In Diffusion in Se

Akhundov (1958) used In^{114} to measure the In diffusion in Se in the 50 °C to 200 ° C temperature range

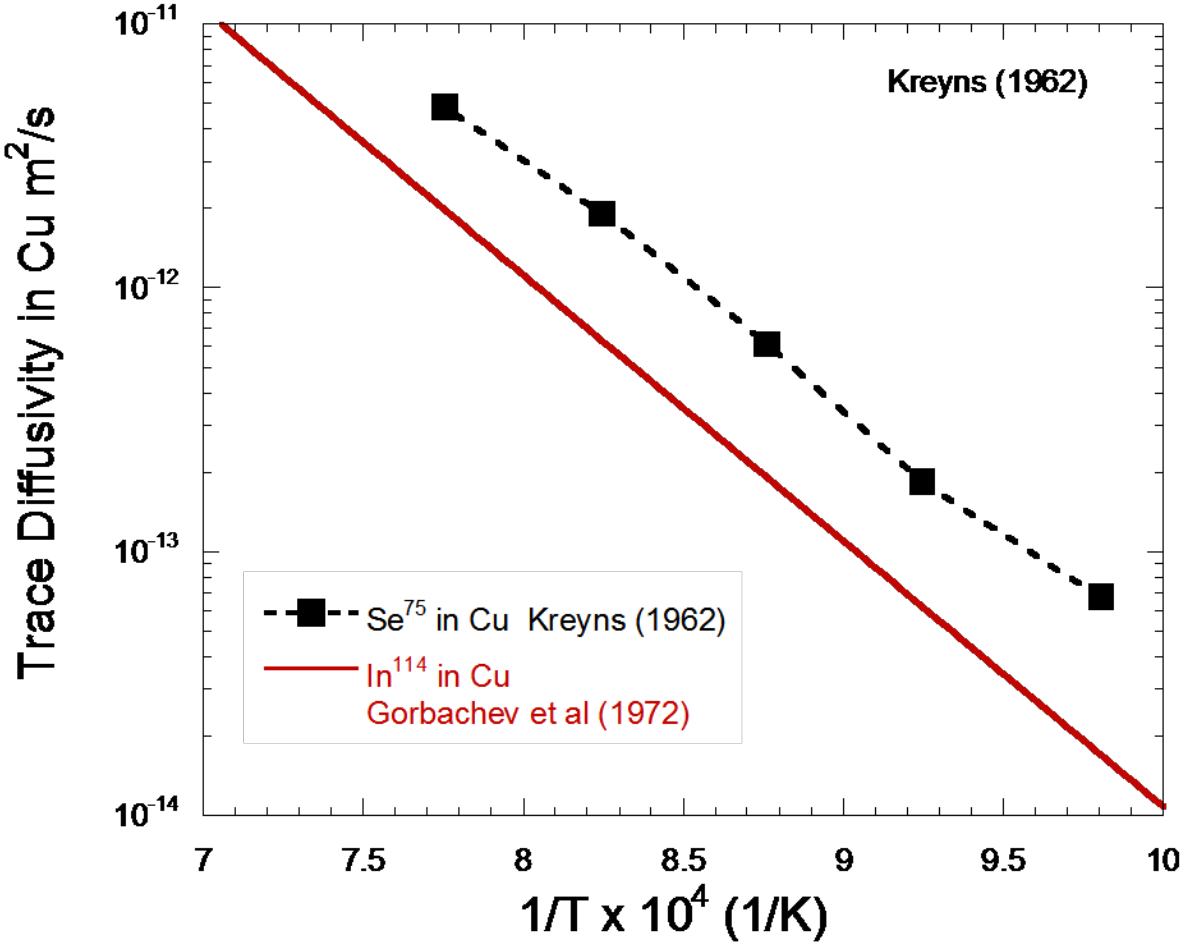


$$D_{In\rightarrow Se} = 5.2\times10^{-6}\exp\left(-\frac{31000}{RT}\right) cm^2\cdot s^{-1}$$

Aknaundov concluded that the low activation energy indicated an interstitial diffusion mechanism. Mostly the measurements are of short-circuit diffusion mechanism (i.e. grain boundary diffusion).

G. A. Akhundov, Thesis (Author's abstract) Izd. Akad. Nauk AzSSR, 1958.

Diffusion in Cu



Se diffusion in Cu is greater than In in Cu.

$$D_{In\rightarrow Cu} = 1.3 \pm 0.15 \exp\left(-\frac{193000}{RT}\right) cm^2 \cdot s^{-1}$$

•V. A. Gorbachev et al. Fiz. Met. Metalloved 34 (1972) 879-83.

•P. H. Kreyns, The Diffusion of Radioactive Tracer Se^{75} into Copper Single Crystal, (MS Thesis) U. Arizona, (1962).

Cu Diffusion in Cu_2Se

Measured by Hauffe (1955)

$$D_{Cu \rightarrow Cu_2Se} = 3.5 \times 10^{-2} \exp\left(-\frac{29000}{RT} \right) cm^2 s^{-1}$$

Low activation energy indicates some type defect-controlled diffusion mechansim

Maymyko Pavlyuchenko and Pokrovskii (1972) studied Cu diffusion in $Cu_{2-x}Se$ between 150 °C and 445° C.

$$D_{Cu \rightarrow Cu_2Se} = 1.3 \begin{matrix} +0.8 \\ -0.5 \end{matrix} \times 10^{-4} \exp\left(-\frac{3130 \pm 600}{RT} \right) cm^2 s^{-1}$$

$$D_{Cu \rightarrow Cu_{1.8}Se} = 8.5 \begin{matrix} +6.3 \\ -3.6 \end{matrix} \times 10^{-4} \exp\left(-\frac{3960 \pm 600}{RT} \right) cm^2 s^{-1}$$

K. Hauffe, “Reaktionen in und an feston Stoffen.” Berlin, 1955.

S. G. Maymyko, M.M. Pavlyuchenko and I.I.Pokrovskii, Dolk. Akad. Nauk.Beloruss. SSR 16 No 6 (1972) 521-3.

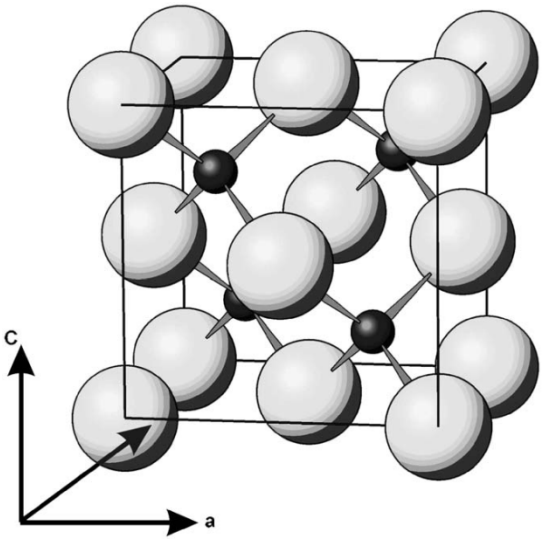
Diffusion in $Cu_{2-x}Se$

(Cu,Va) (Cu,In) Se

Reinhold and Möhring (1937) measured the diffusivity of Cu^{+1} ions in $Cu_{2-x}Se$ where $0.11 < x < 0.22$.

$$D_{Cu^{+1} \rightarrow Cu_{2-x}Se} = 5.6 \times 10^{-4} cm^2 s^{-1} \text{ at } 723 \text{ K}$$

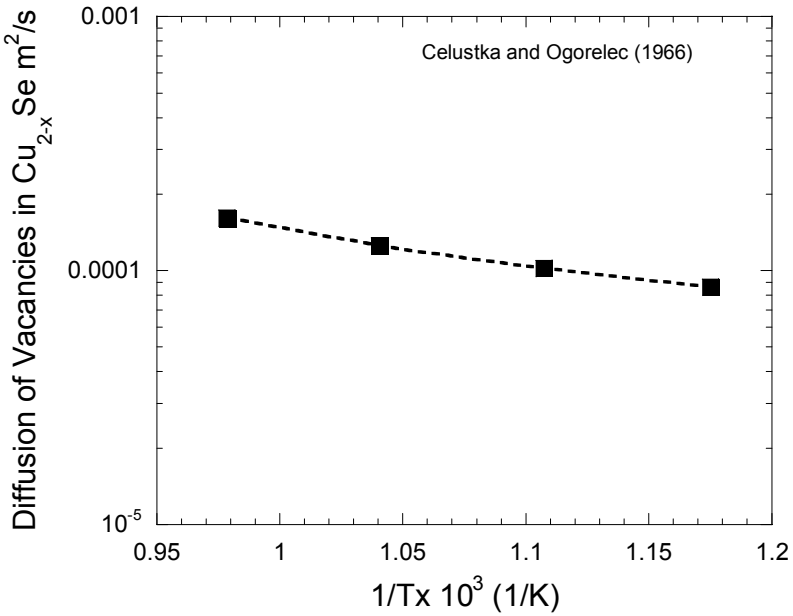
$$D_{Cu^{+1} \rightarrow Cu_{2-x}Se} = 0.2 \times 10^{-4} cm^2 s^{-1} \text{ at } 298 \text{ K}$$



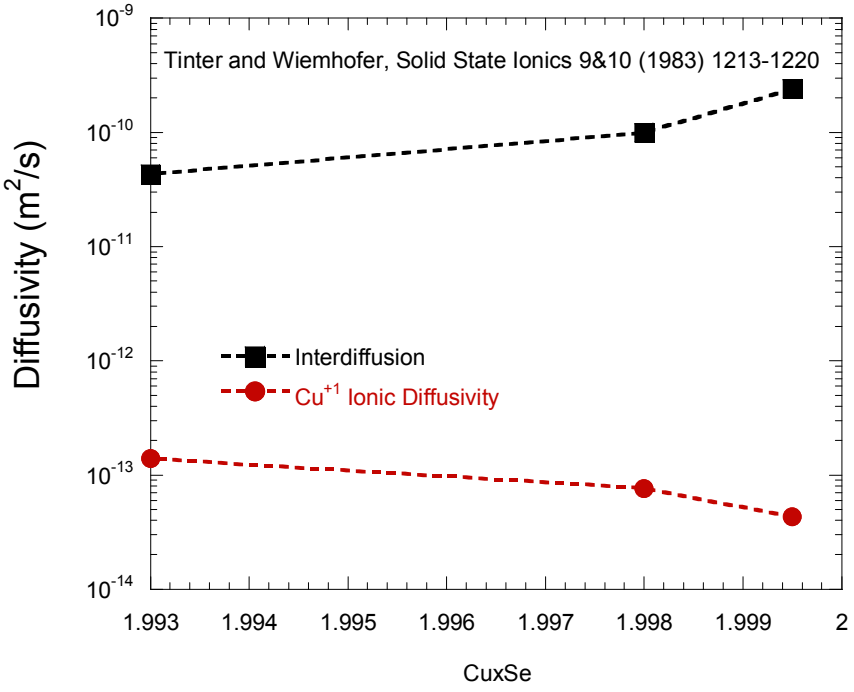
The zincblende sublattice of β-Cu2Se. The cations and Se2 anions are each stacked like ABC along the /111S direction. Cu+: dark, Se2: bright balls.

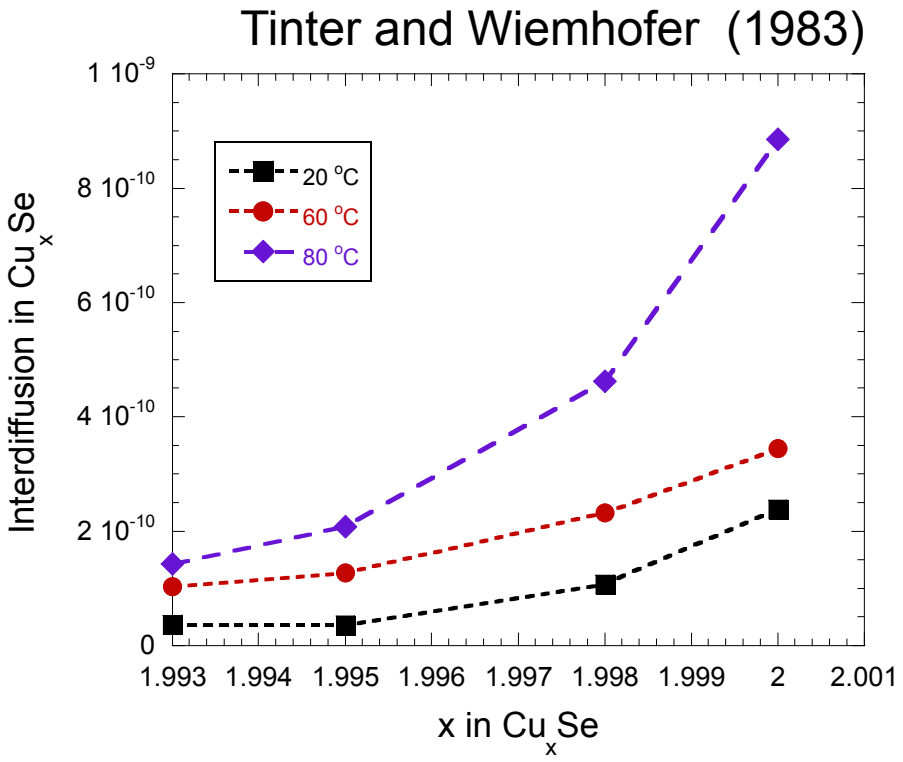
Čelustka and Ogorelec measured the diffusion of vacancies in $Cu_{1.96}Se$ from 500 °C to 850 °C

$$D_{Va \rightarrow Cu_{2-x}Se} = 0.36 \exp\left(-\frac{34700}{RT}\right) cm^2 s^{-1}$$



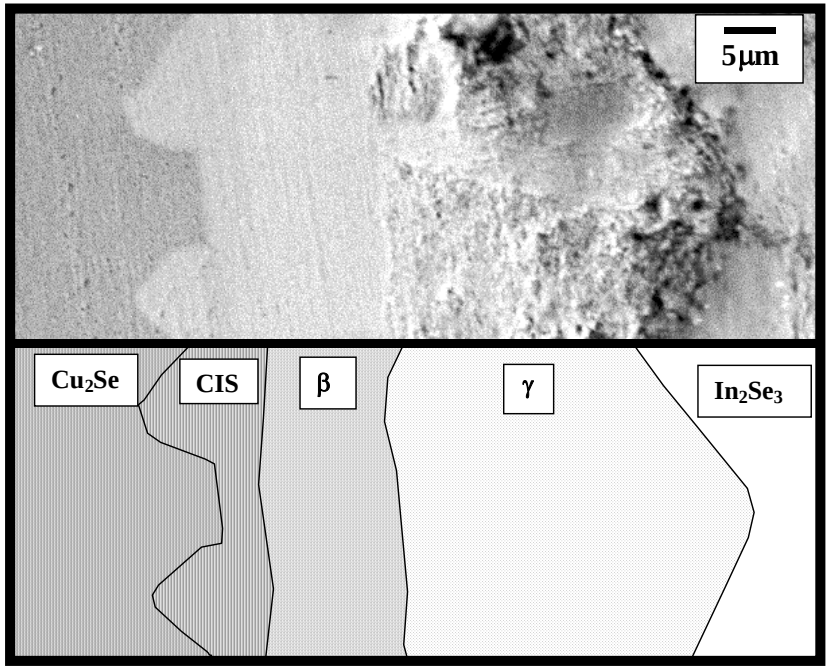
Diffusion in Cu_xSe

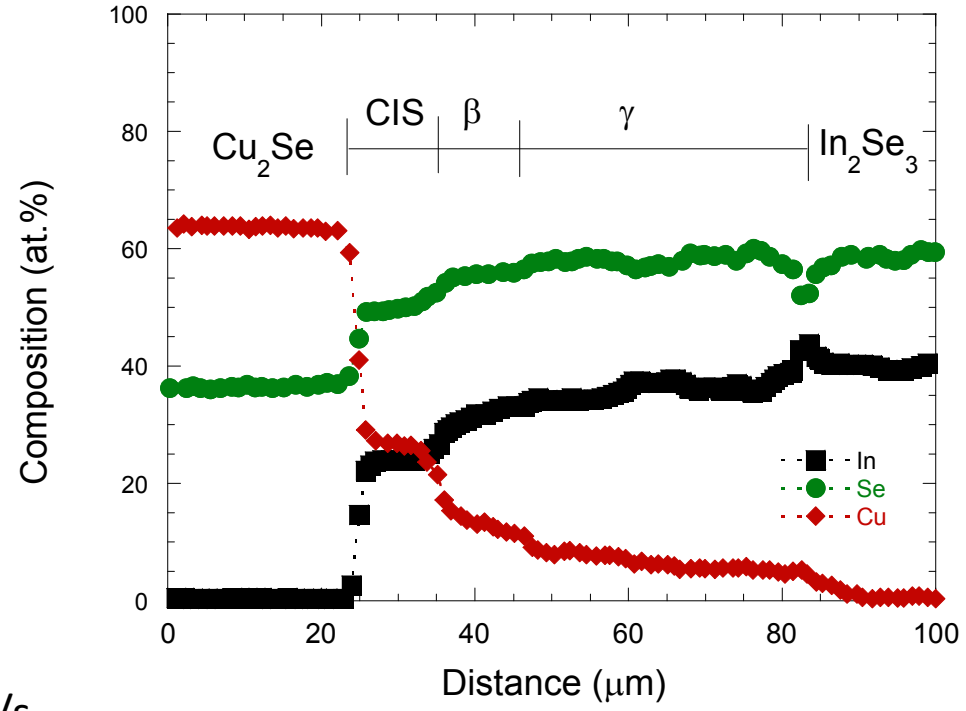




Cu_2Se/In_2Se_3 Diffusion Couple at 550 °C for 1.5 h

CIS = $CuInSe_2$
β= defect chacopyrite ($CuIn_3Se_5$)
γ = $CuIn_5Se_8$

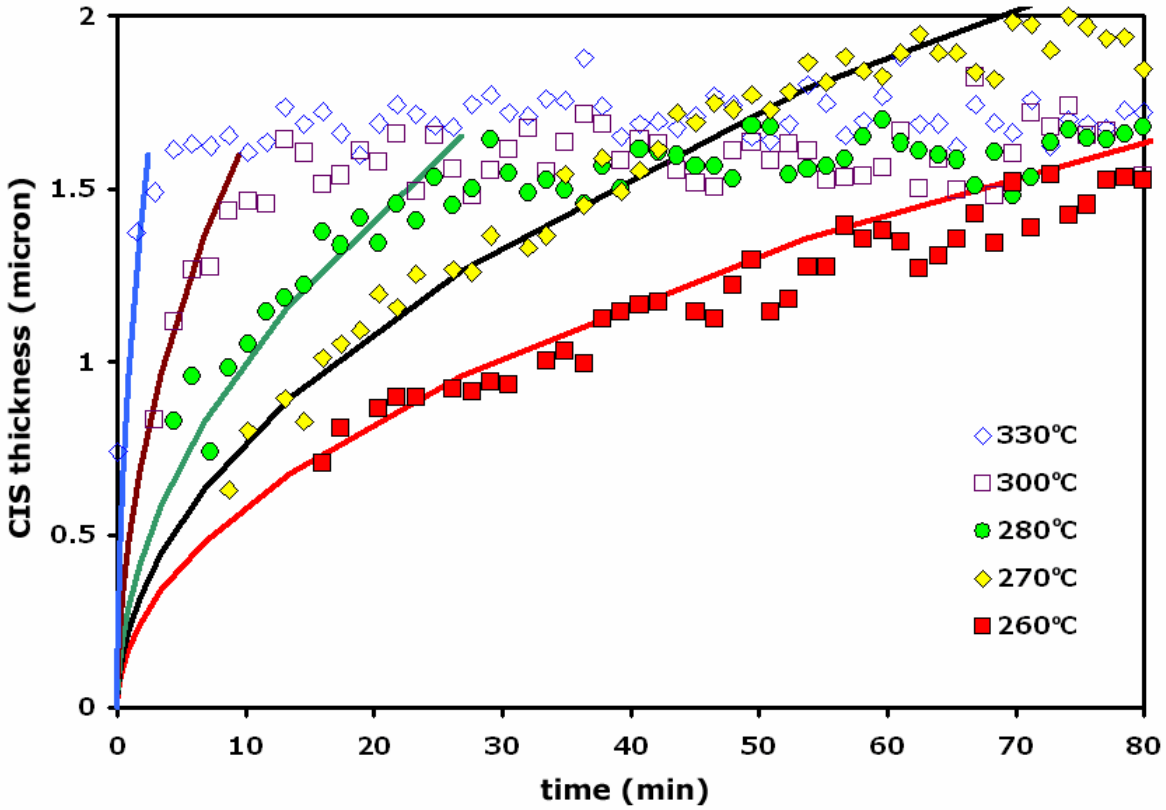




Estimate of In diffusion in Cu_2Se =4.2x10^{-10} m^2/s
Defect structure leads to rapid diffusion.
In diffuses via an ionic lattice diffusion through the Cu vacancy sites on Cu_2Se

Park et. al. , J. Appl. Phys. 87 (2000) 3683.

Mobility of Se in CIS



Activation Energy = 146,725 J/mole
Frequency Factor = 0.01406 m^2/s

The comparison of CIS growth rates between the DICTRA prediction (solid lines) and experiments (symbols).

W. K. Kim , U. Florida, PhD Thesis, 2006.

Interdiffusion in $CuInSe_2$

Tell and Bridenbaugh measured the interdiffusion in $CuInSe_2$ by measuring a junction depth as function of time.

$$\widetilde{D}_{CuInSe_2} = 5.5\times10^{-14}\, m^2 s^{-1} \text{ at } 473\,\text{K}$$

$$\widetilde{D}_{CuInSe_2} = 1.4\times10^{-14}\, m^2 s^{-1} \text{ at } 573\,\text{K}$$

Interdiffusion thought to occur either by

- Se vacancies acting as shallow donors
- Cu interstitials

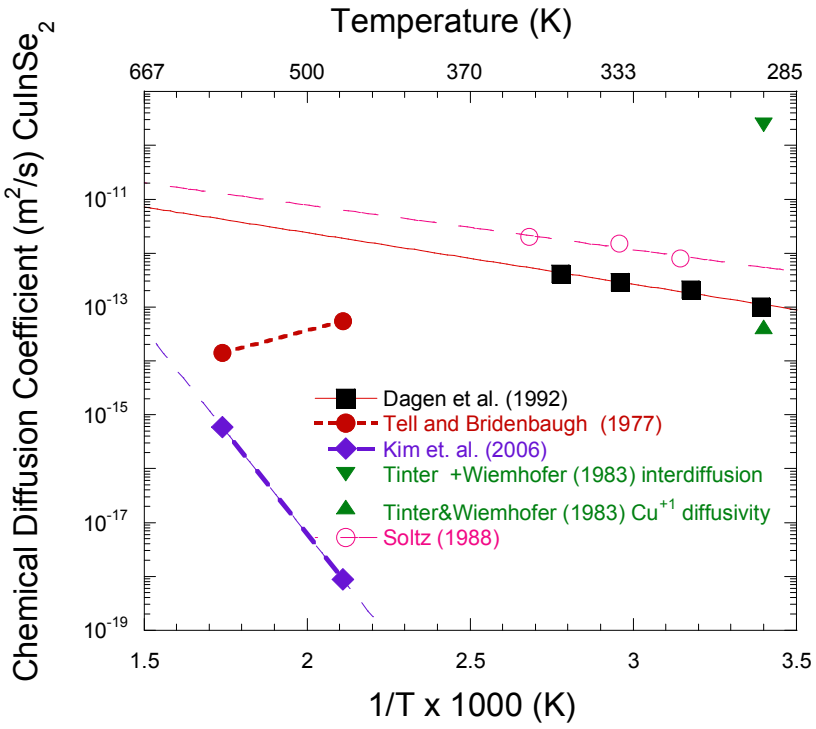
Compare with Kim's functions

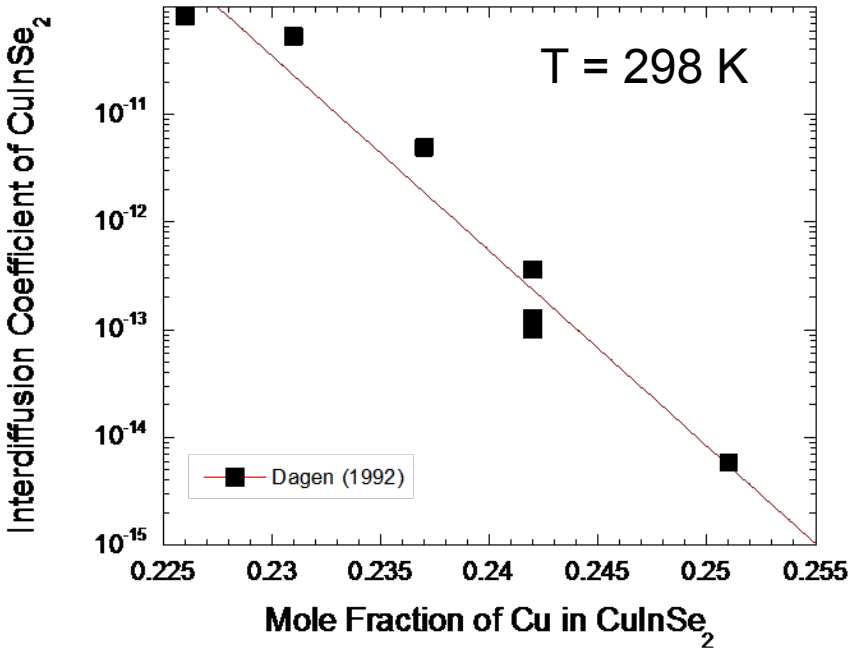
$$D_{Se\rightarrow CuInSe_2} = 8.8\times10^{-19}\ m^2 s^{-1} \text{ at } 473\,\text{K}$$

$$D_{Se\rightarrow CuInSe_2} = 5.9\times10^{-16}\ m^2 s^{-1} \text{ at } 573\,\text{K}$$

Tell and Bridenbaugh, J. Appl. Phys. 48 (1977) 2477.

Interdiffusion in $CuInSe_2$

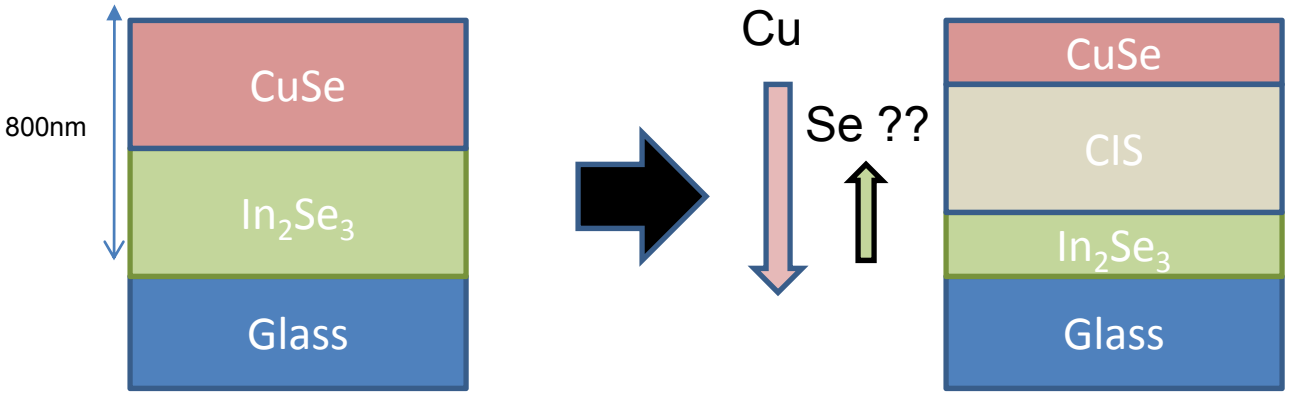




Kim's work

J. Phys. +Chem Solids, 2005. : CuSe/In_2Se_3 precursor

- CIS + Se (evaporated)

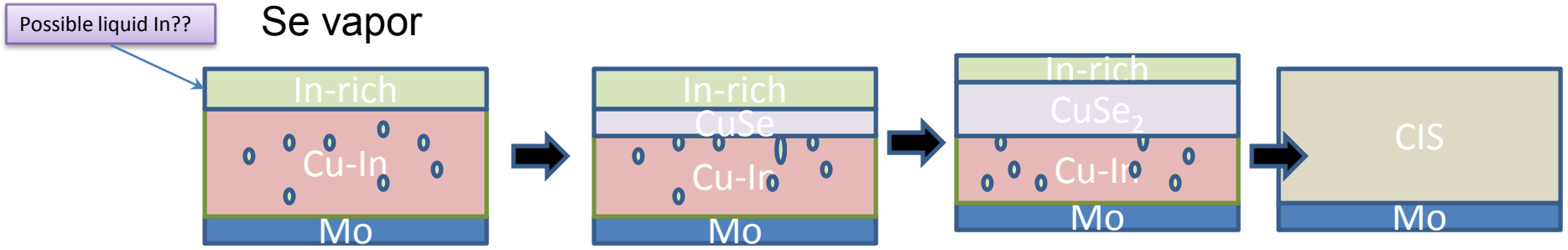


Are these schematics close to the microstructures we are trying model? Are the layers planar?

Activation energy 162 +/- 5 KJ/mol (parabolic model)

J. Crystal Growth , 2005. : Cu/In selenization

- CuSe +In + *n*Se (vapor) → CuSe2 +In +*n*Se (vapor) → CIS

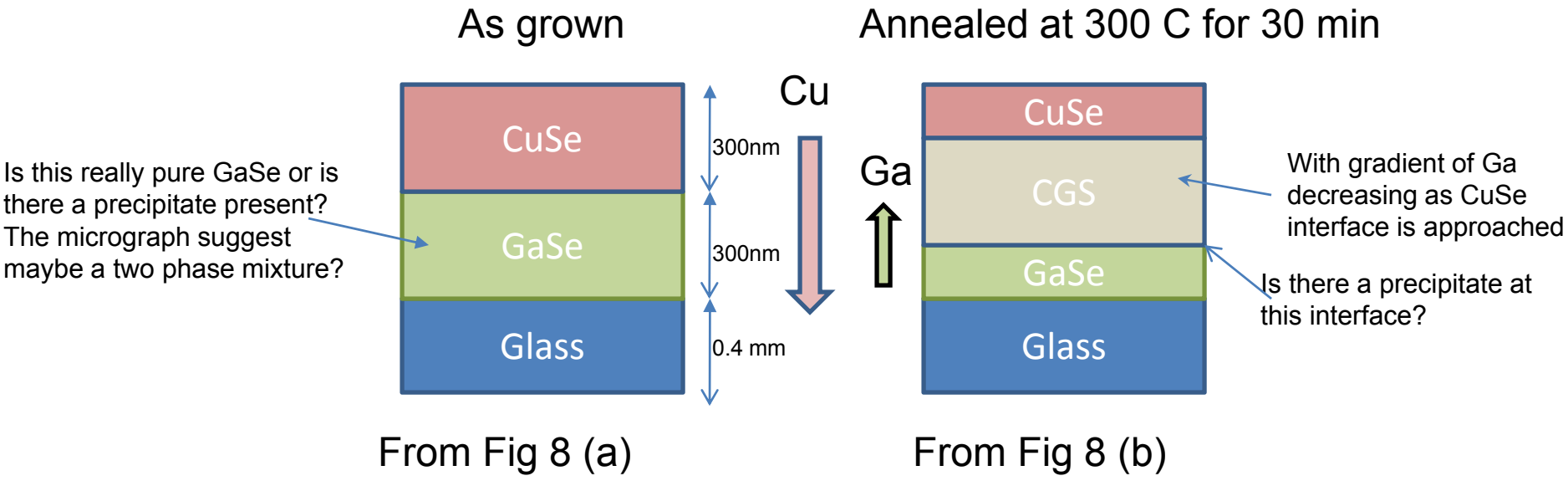


Activation energy 124 +/- 19 kJ/mol (Avrami model); 100 +/- 14 kJ/mol parabolic

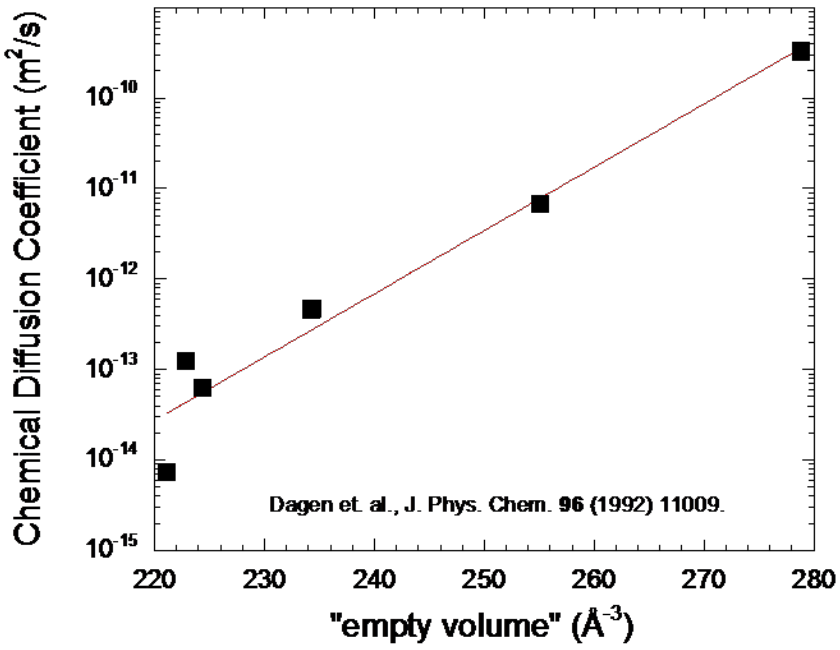
Kim's work

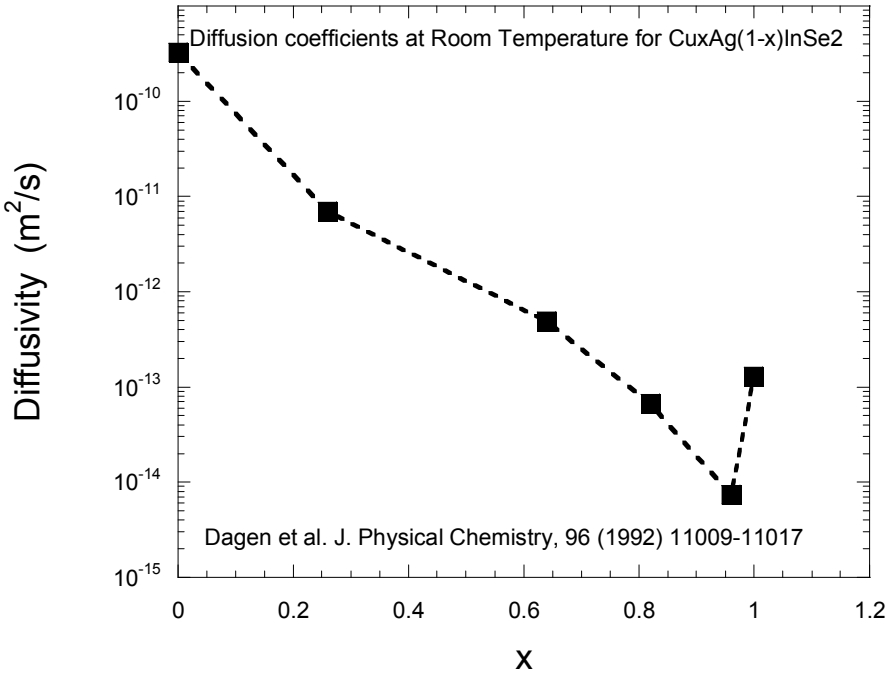
- Summary of reaction pathways and activation energies in J. Crystal Growth 2008, Table 2.

J. Crystal Growth, 2008. : GaSe/CuSe precursor
• GaSe (amorph.) +1/2$Cu_{2-x}Se$+1/2Se →CGS



Interdiffusion in $Cu_xAg_{1-x}InSe_2$





Empty volume per unit cell at room temperature

Diffusion studies

- Djessas et. al. J. Appl. Phys. 95 (2004) 4111.
  - Studied interdiffusion of Cu, In, Ga diffuse through $In_2Se_3/CuGaSe_2/SnO_2$
  - Experimental setup
    - $CuGaSe_2$ layers grown using close-space vapor transport. Two different grain sizes
    - In_2Se_3 deposited by thermal evaporation on $CuGaSe_2$ at a low substrate temp.
    - Heterostructures annealed at different temperatures
    - Concentration profiles measured using SIMS
  - Results
    - Cu diffuses through $CuGaSe_2$ layer to the In_2Se_3
    - In diffues from In_2Se_3 through $CuGaSe_2$ to SnO_2
    - Cu diffusion in the In_2Se_3 layer is probably grain boundary diffusion
    - Cu and In diffusion away from $In_2Se_3/CuGaSe_2$ interface mostly likely grain boundary diffusion.

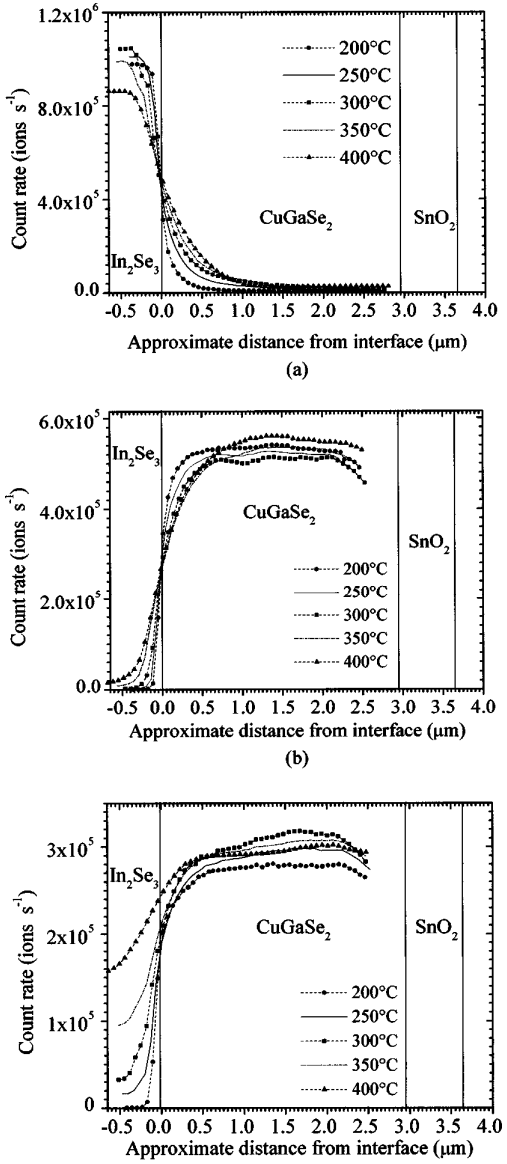
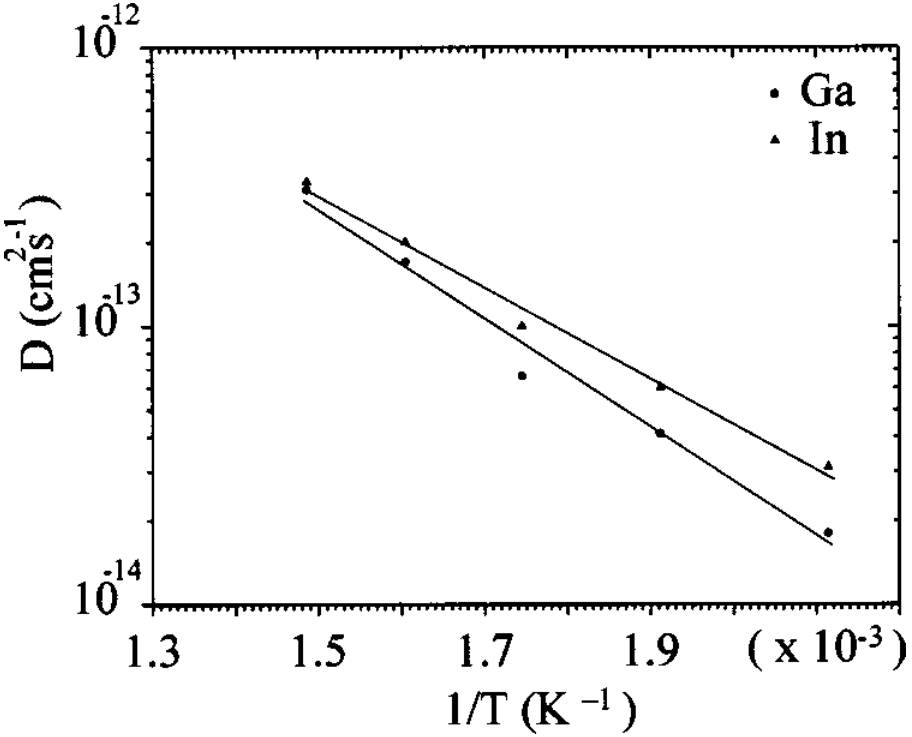


FIG. 1. Indium ~a!, gallium ~b!, and copper ~c! SIMS concentration profiles in an In2Se3 /CuGaSe2 /SnO2 /glass type I structure annealed in vacuum for 20 min at different temperatures.

In and Ga diffusion coefficients at a $In_2Se_3/CuGaSe_2$ interface



Element	Activation Energy (kJ/mole)	Frequency Factor (cm^2s^{-1})
Ga	36.6	$2.2x10^{-10}$
In	30.8	$8.1x10^{-10}$

Indicate possible grain boundary diffusion

FIG. 2. In and Ga diffusion coefficients in terms of the reciprocal temperature.

Djessas et. al. J. Appl. Phys. 95 (2004) 4111

Diffusion notes

- J. Djordjevic, J. Crystal. Growth 294 (2006) 218-230.
  - Vapor selenization of Cu layers
    - Cu diffusion coefficient in $Cu_{2-x}Se$ is orders of magnitude higher than Se in $CuInSe_4$
    - Rate determining step is surface reaction and not Cu diffusion
  - In selenization
    - Control by In diffusion through layers $In_4Se_3 \rightarrow InSe \rightarrow In_2Se_3$
    - Se incorporated at the surface of the growing film
  - $CuInSe_2$ from $Cu_{xl}n$ precursors: two reaction paths depending on Cu/In
    - In diffusion into $Cu_{2-x}Se$
    - reaction of InSe and $Cu_{2-x}Se$

- Diffusion data by Lyubormirsky, Dagen and Klenfeld all indicate some dependence on
  - Ionic conductivity (concentration and mobility)
  - p vs n conductor

- Diffusion measurements dependent on type measurement made: (Lybormirsky et al. 1998) -- need watch out when using published data.
  - Tracer diffusion measurements (concentration gradient)
  - p-n junction methods (~ two order of magnitude higher than tracer diffusion)
  - Potentiostatic current decay method (higher than p-n junction) methods

Diffusion Notes

- F. Herget et. al. (Phys. Stat. Sol. A 203 (2006) 2615.) Chemical solid-state reactions promoted by epitaxy.
  - Need epitaxial relation to exist, for ion diffusion to start.
  - If a redox reaction is energetically favorable, it will occur as a 2^{nd} step. (electron exchange must occur first)
  - Ion diffusion is easier if one structure is ion conductive
  - CuSe+ GaSe $\rightarrow$ $CuGaSe_2$
    - Assuming the anion sublattices of all 3 compounds are equal, then only have cations redistribute via interdiffusion.
    - Cation radii << anion radii, so diffusion is relative fast.
    - $1/2\beta{-}Cu_2Se$ +InSe +1/2Se(liq) $\rightarrow$ $CuInSe_2$ Reaction C (SEL) of (Hergert et al. J. Solid State Chem. 179 (2006) 2394.)
      - Driven by In^{+3} diffusion

How to Proceed??

- Diffusion in solid solutions ✓
- Diffusion in stoichiometric phases: binaries ok, but need data
- Diffusion in ternary compound phases
  - α $CuInSe_2$ (Cu%,In,Va)(Cu,In%,Va)Se_2 (Chacopyrite) ????
  - Are the current thermodynamics adequate to deal with the diffusion accurately?? Some question about needing to treat the charged species?