Radiotracer diffusion of copper and potassium in $Cu(In,Ga)Se_2$ (CIGS) thin-film solar cells

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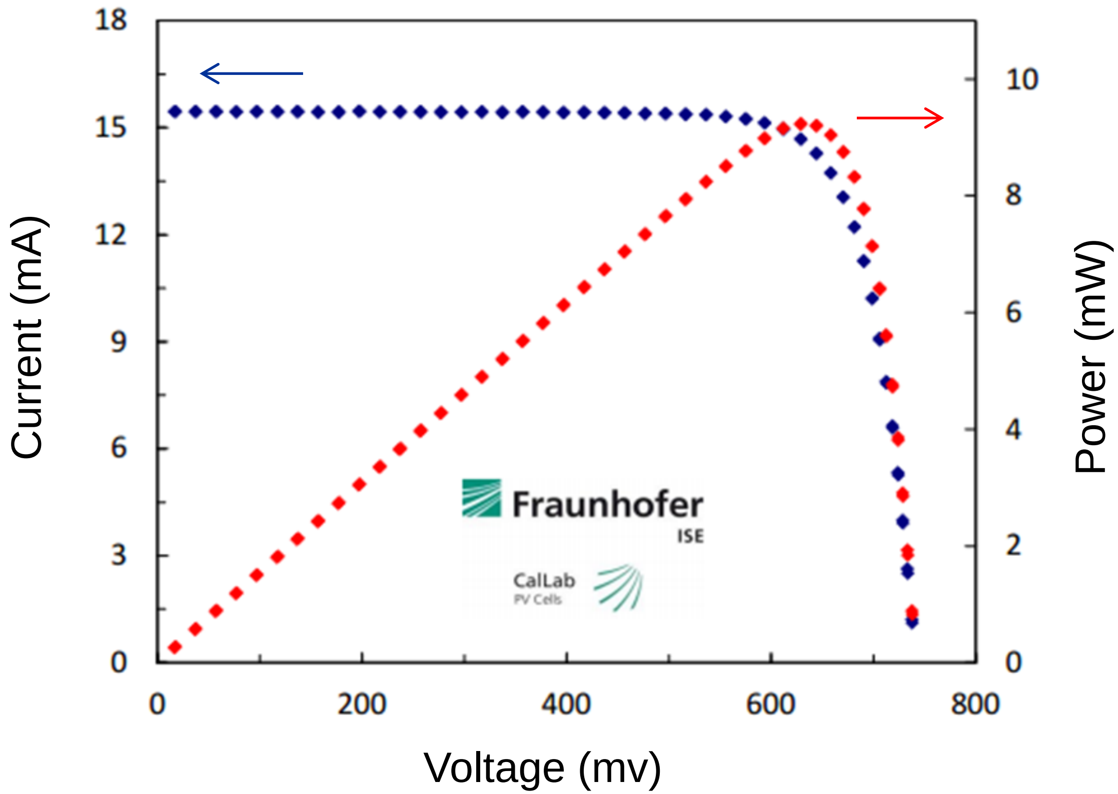
Westfälische Wilhelms-Universität Münster

- *INTC-P-476*
- *CERN-INTC-2016-043*

2015: New World Record for CIGS Solar Cells:

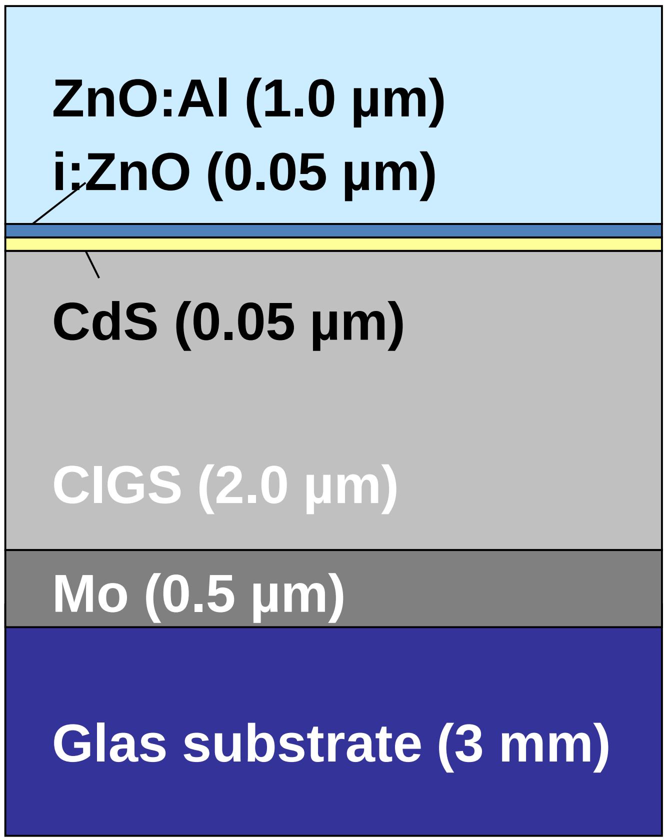
22.6% certified

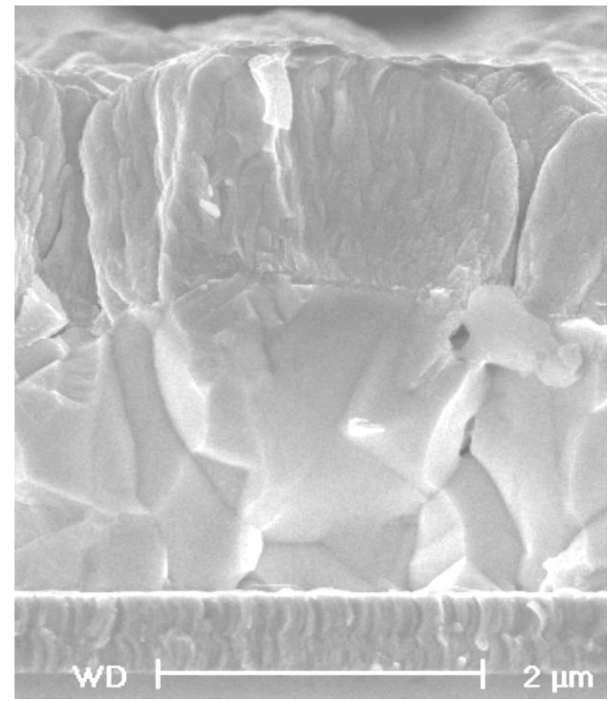


$\eta_{cert.}$	=	**22.6 %** with ARC
V_{oc}	=	741 mV
FF	=	80.6 %
j_{sc}	=	37.8 mA/cm²

Improvement due to K used in addition to Na as the standard „doping“ element

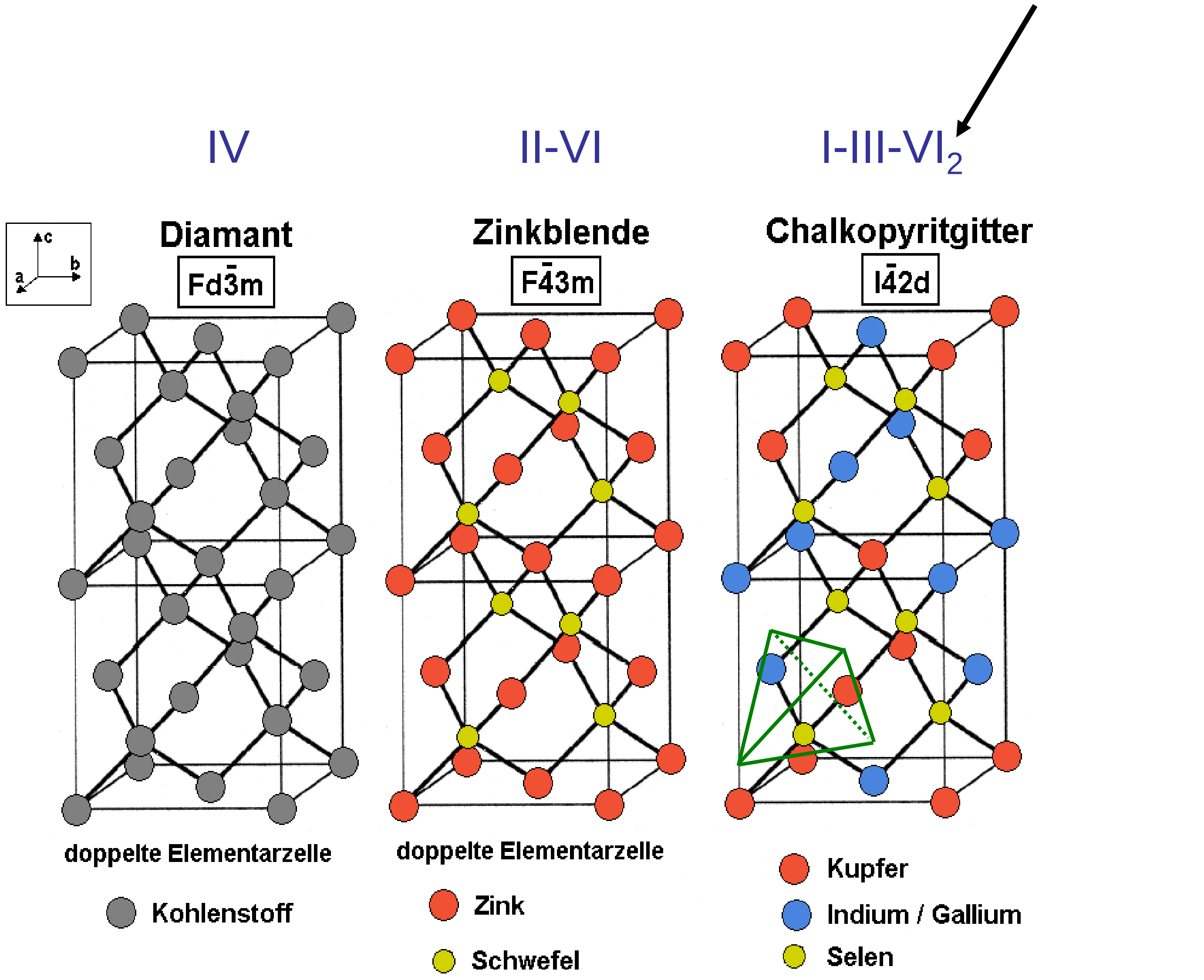
Solar Cell Structure





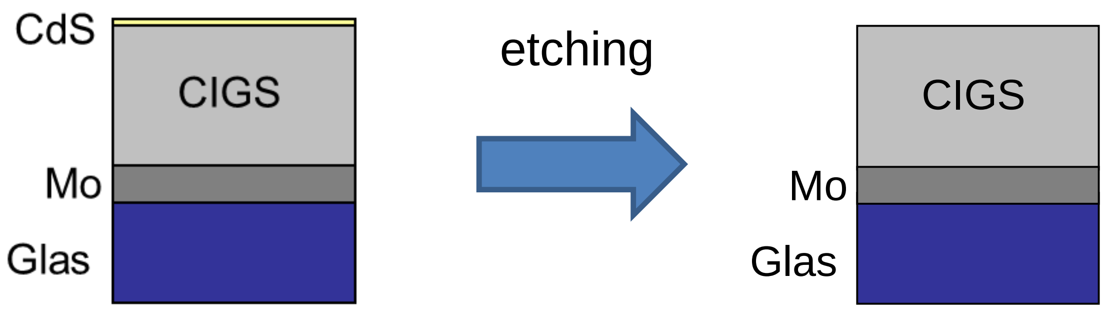
Polycrystalline CIGS layers:
d ≈ 2 µm

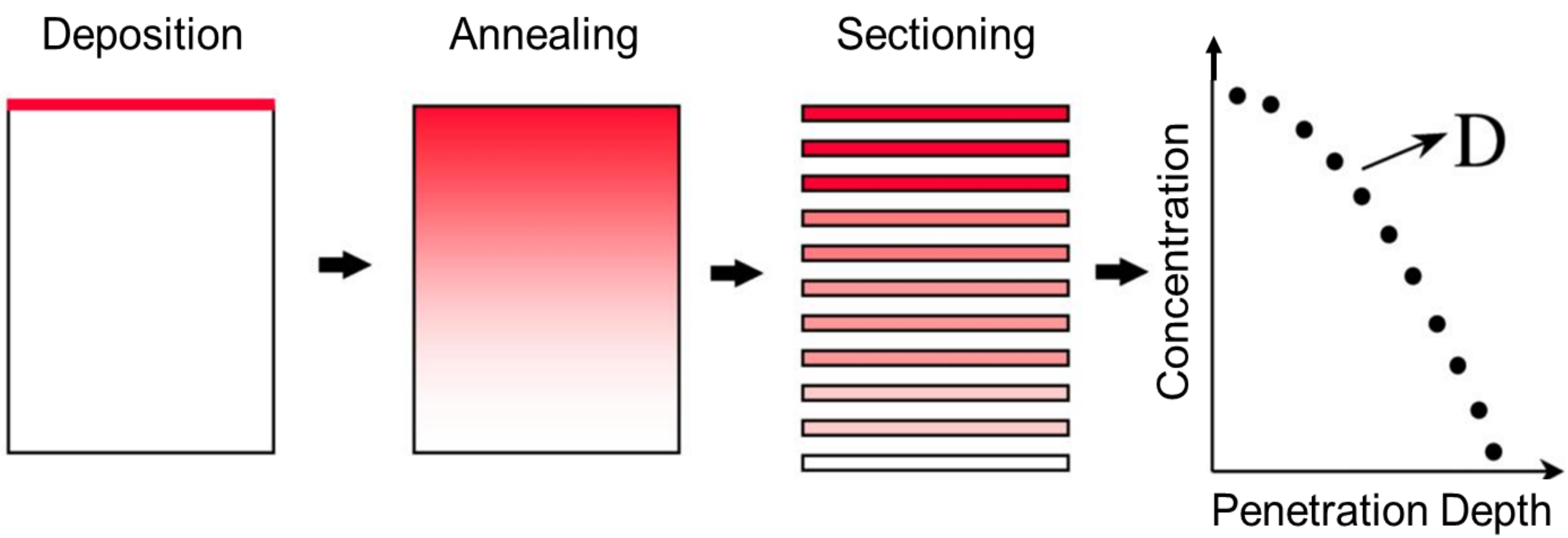
$Cu(In,Ga)Se_2$ Crystal Structure



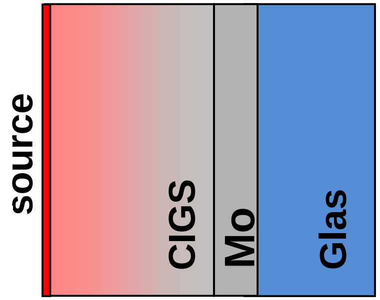
Diffusion Exps. in CIGS: Radiotracer Technique

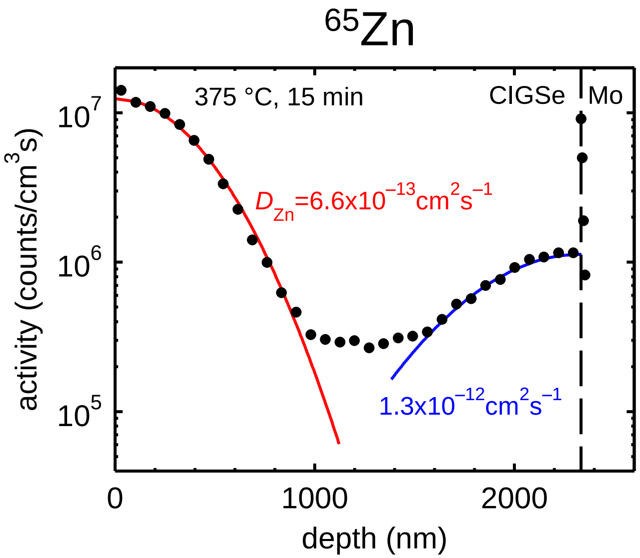
Important for optimizing CIGS processing and solar-cell efficiency

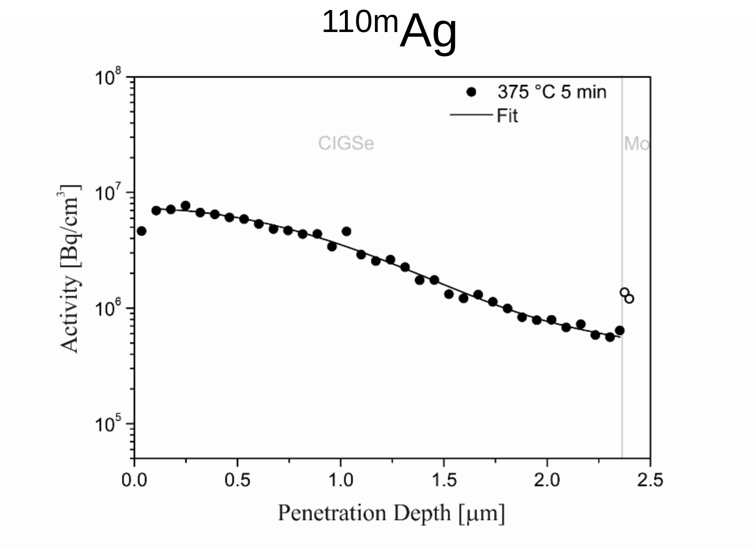




Diffusion Profiles of ^{65}Zn & ^{110m}Ag in CIGS

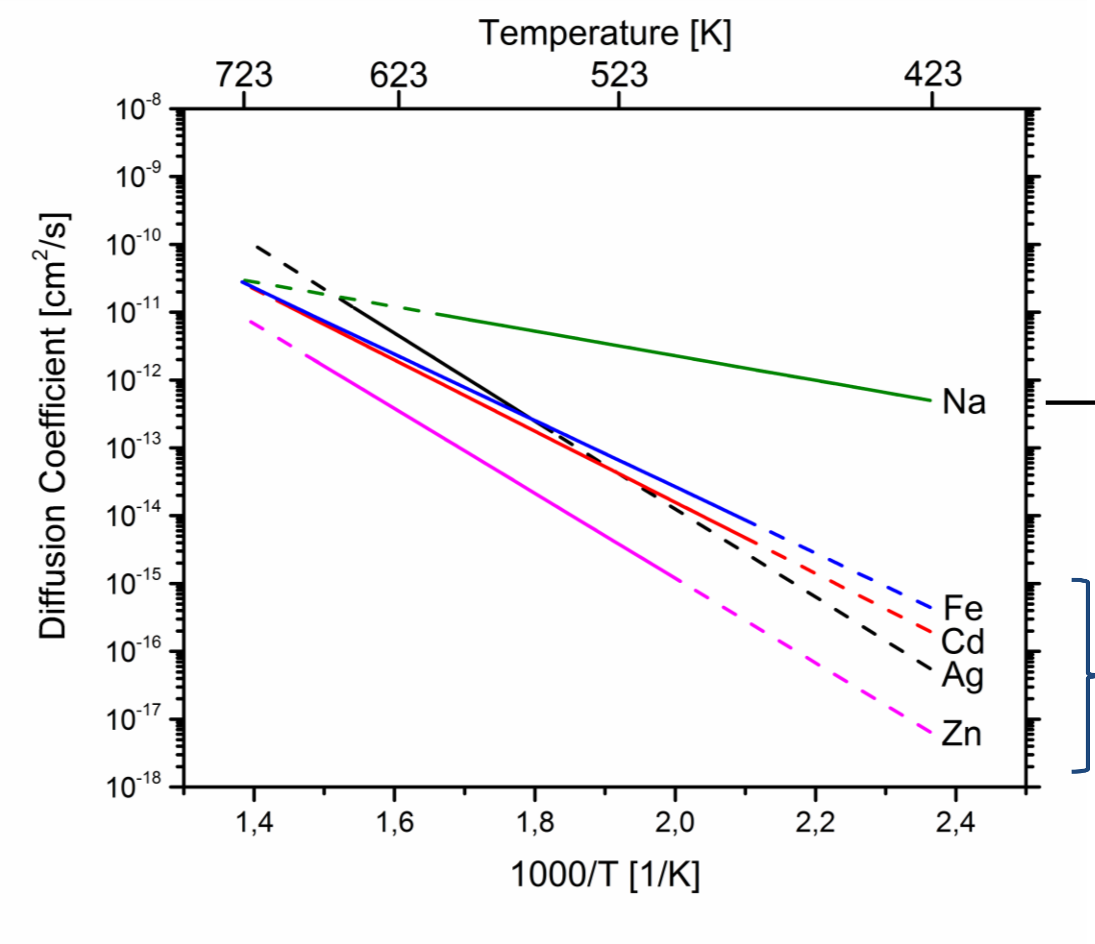






Zn = **front-layer** element: ZnS buffer / ZnO transparent oxide
Ag = **alloying** element: substitute for Cu in (Cu,Ag)(In,Ga)Se_2

Master Plot: Impurity Diffusion in CIGS



ZSW Stuttgart

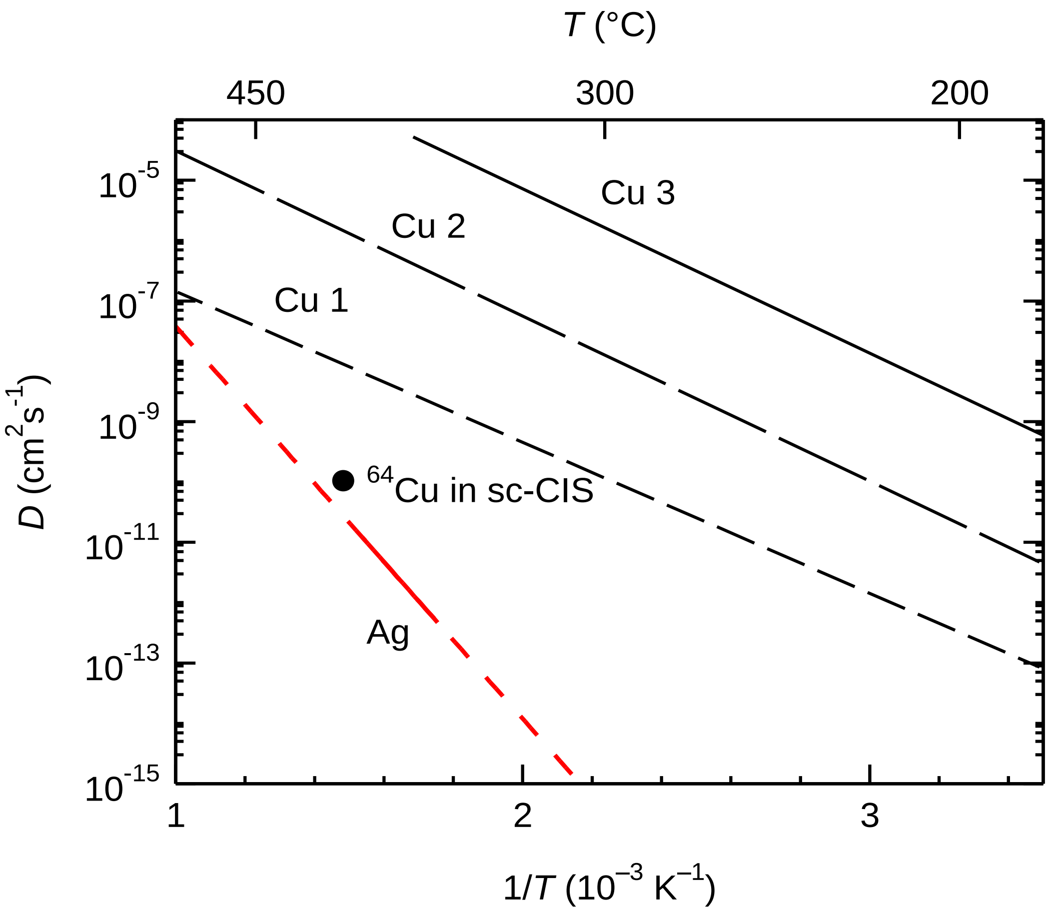
Münster group

accommodated by
Cu sublattice

Cd = **front-layer** element: standard CdS buffer layer
Fe = **substrate** element: steel foil as flexible substrate
Na = **beneficial** impurity: improves solar-cell efficiency

Cu diffusion in CIGS

Self-diffusivity on Cu sublattice important for interpretation of impurity diffusion



Lubomirsky et al., JAP 83 (1998) 4678

Cu 1, Cu 2, Cu 3:

- various authors,
- various (electrical) methods

^{64}Cu:

- tracer experiment
- bulk single-crystal CIS

No reliable data exist for Cu diffusion in CIGS !

Planned Experiment 1: $^{67}Cu/^{64}Cu$ Diffusion in CIGS

Self-diffusivity on Cu sublattice data needed to identify diffusion mechanisms

^{67}Cu:	$t_{1/2}$ = 2.6 d	ϒ = 0.185 MeV	49% abundance
	UC_x target	**3.5×10^8** ions/µC	< **30** min/sample
	ZrO_2	**2.0×10^7**	**30**

Half-life time allows for **double-tracked** experiments:

- **On-site** with ISOLDE/ODC
- **Off-site** at Münster Laboratory (after implantation at ISOLDE)

^{64}Cu:	$t_{1/2}$ = 12.7 h	ϒ = 1.346 MeV	0.5% abundance
	UC_x target	**2.0×10^8** ions/µC	**30** min/sample

- Only **on-site** experiments possible
- ^{64}Cu **less suitable** than ^{67}Cu

Beam request: 3 shifts over 2 years

Planned Experiment 2: ^{43}K Diffusion in CIGS

Potassium data needed to optimize solar-cell efficiency

^{43}K:	$t_{1/2}$ = 22.2 h	ϒ = 0.373 MeV	87% abundance
	UC_x target	**2.4×10^{7}** ions/μC	**30** min/sample

- **On-site** experiments preferable
- Feasibility demonstrated by exps. on feldspar (July 2016)

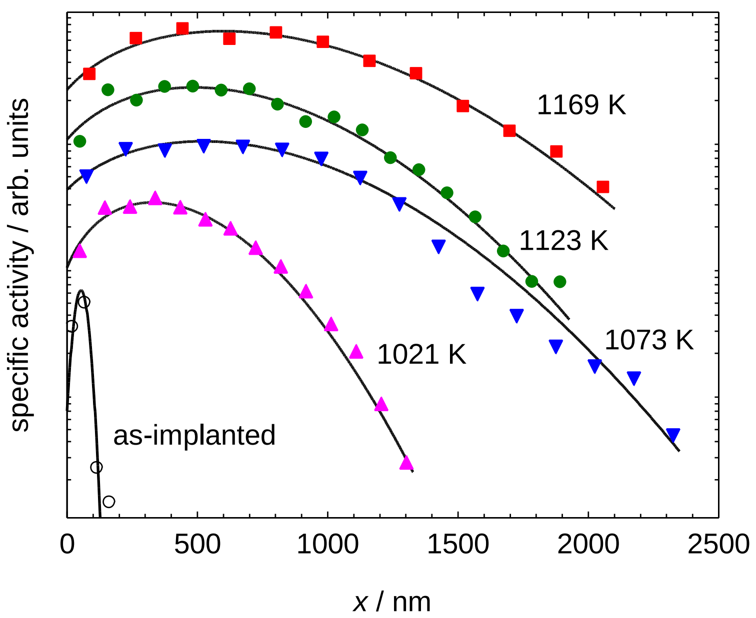
Beam request: 3 shifts over 2 years

^{43}K Diffusion in Single-Crystal Alkali Feldspar ⊥ (001)

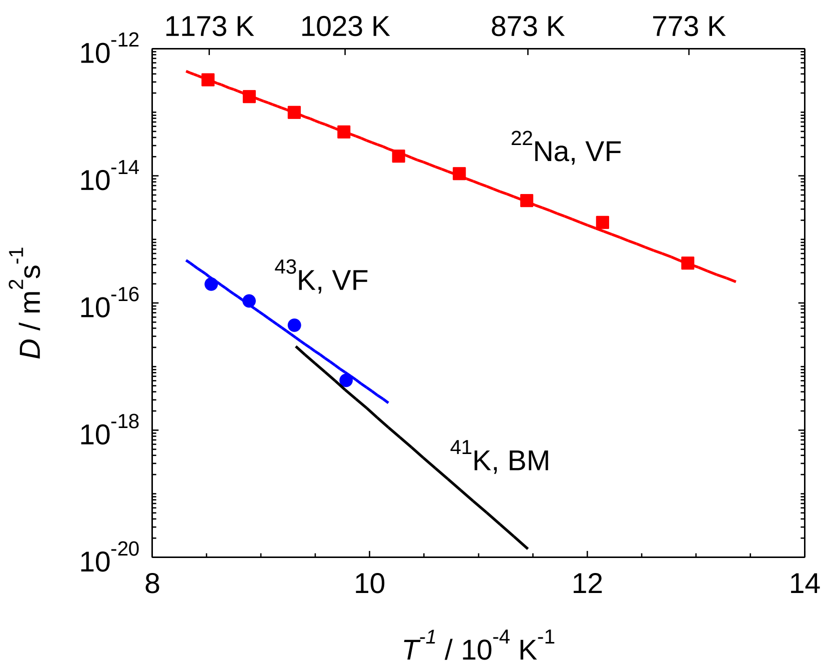
(using ISOLDE/ODC facilities, July 2016)

- *F. Hergemöller, M. Wegner et al., Phys. Chem. Minerals, submitted*

Diffusion profiles



Diffusion coefficients



VF = Volkesfeld (Eifel, Germany), single crystal ⊥ (001)
BM = Benson Mines (USA), randomly oriented grains

Conclusion:
$D_K << D_{Na}$

On-line Diffusion Chamber (ODC) ... to be used in Off-line modus

Concept & Construction: Saarbrücken Group

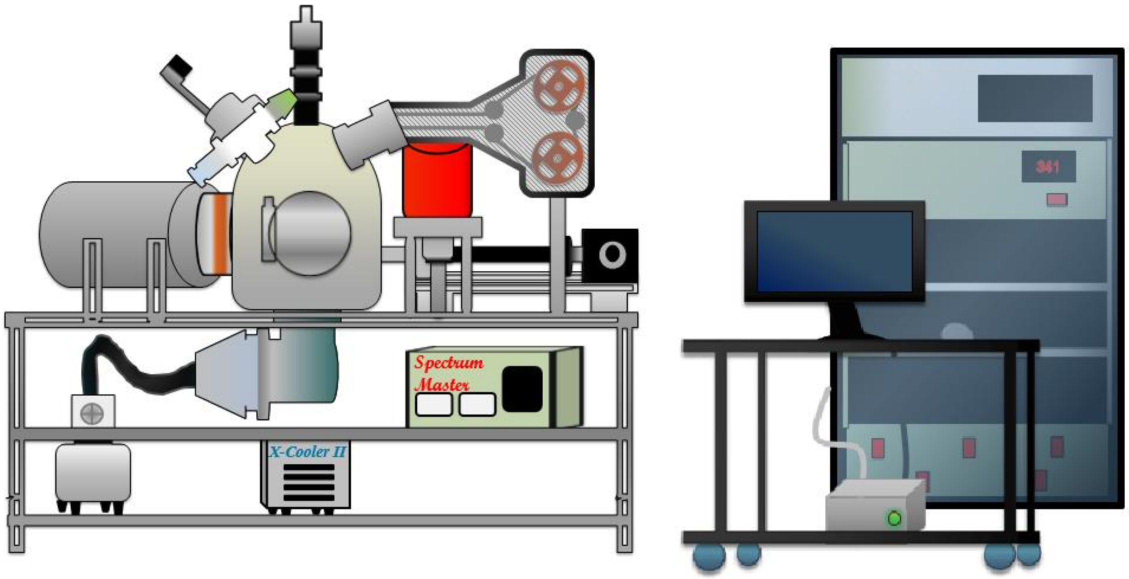


Figure 1. A representation of the ODC's set-up and the location of its peripherals.

User Guide: Jaime E. Avilés Acosta

Resumé

- Overall request: **6 shifts over 2 years**
- Our offer: **support for ODC maintainance** by Münster groups

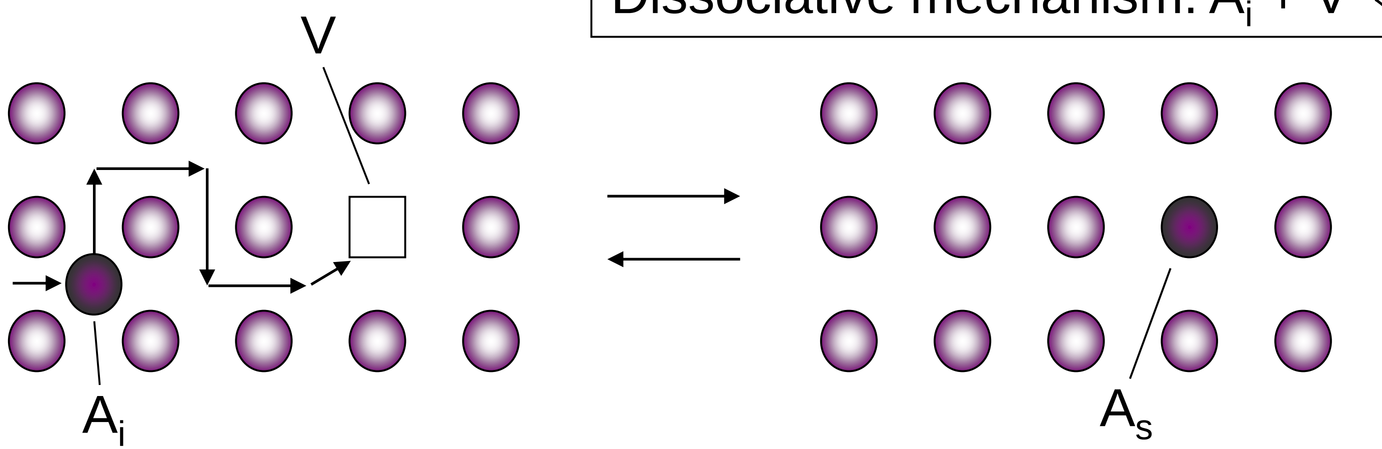
With thanks to:

- **Saarbrücken group:** Manfred Deicher, Herbert Wolf
- **ISOLDE team:** Karl Johnston, Juliana Schell

Interstitial-Substitutional Diffusion

(Prominent in **semiconductors** such as Ge, Si, GaAs, etc.)

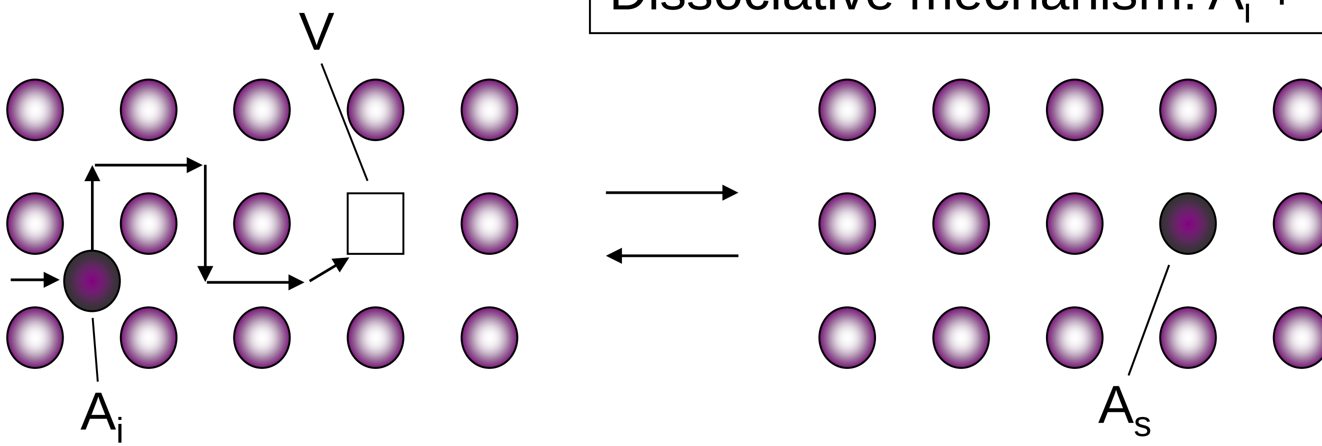
Dissociative mechanism: $A_i + V \Leftrightarrow A_s$



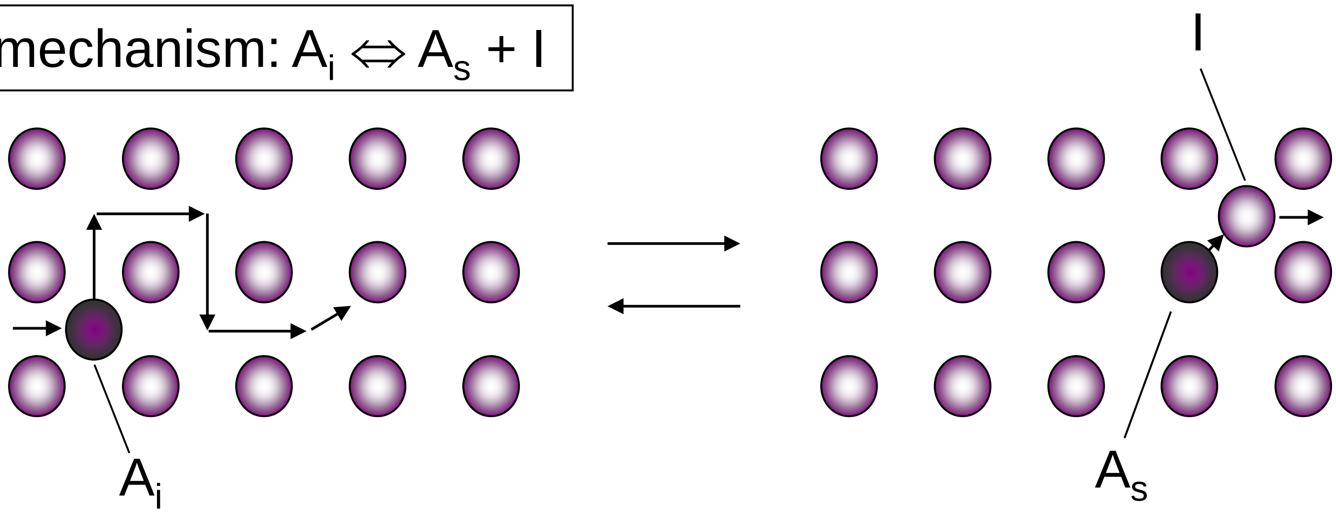
A_i = minority species, fast interstitial, responsible for impurity transport
A_s = majority species, virtually immobile, determines solubility (C_s^{eq})
V = vacancy, mediates interstitial-substitutional exchange

Interstitial-Substitutional Diffusion

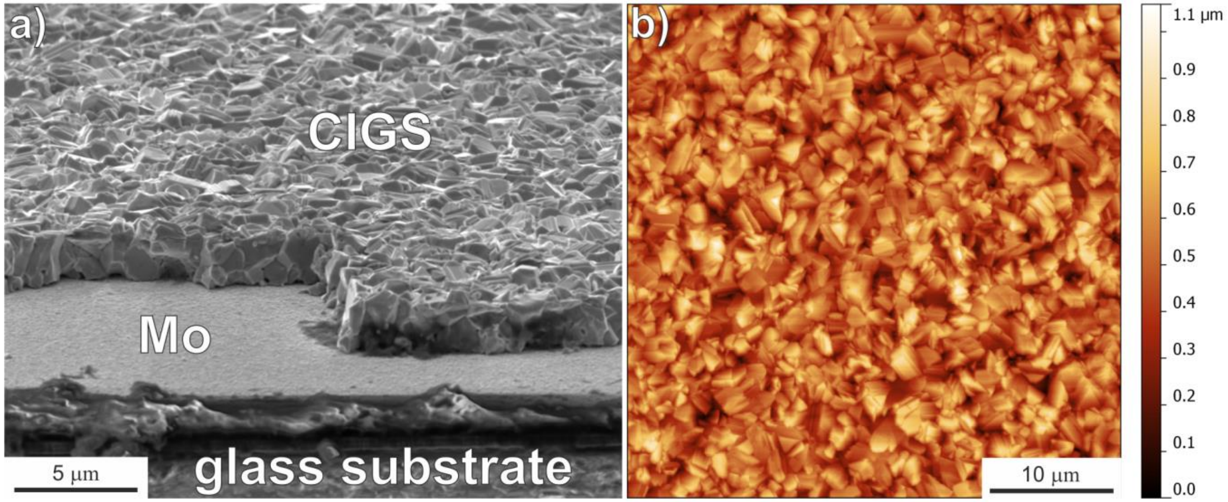
Dissociative mechanism: $A_i + V \Leftrightarrow A_s$



Kick-out mechanism: $A_i \Leftrightarrow A_s + I$



CIGS Layer & Surface Structure



(a) **Side view SEM image of the CIGSe/Mo/soda-lime glass layer structure of a diffusion sample. The CIGS layer thickness is 2.34 mm and the grain size is approximately 2 µm**

(b) **AFM measurement of the surface topology of the CIGSe layer (R_{RMS} ~ 140 nm).**

Solar Cell Record Efficiencies

c-Si = 25.6 %[1)]

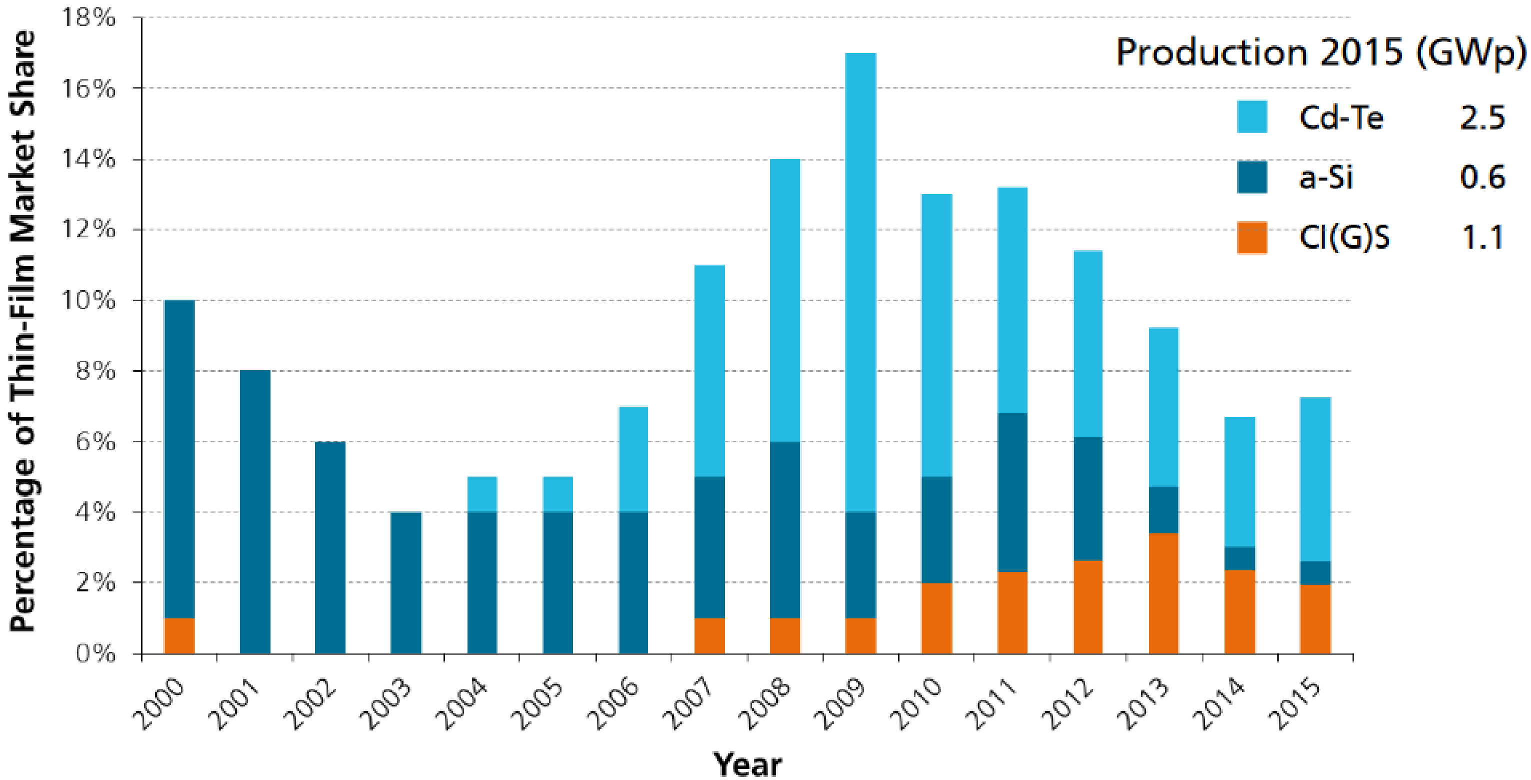
mc-Si = 20.8 %[1)]

CIGS = 22.6 %[2)]

CdTe = 22.1 %[3)]

1) M. A. Green et al., Progress in Photovolt. Res. Appl. 23 (19015) 805
2) P. Jackson et al., Phys. Status Solidi RRL, 10 (2016) 583
3) www.firstsolar.com

Market Share of Thin-Film Technologies
Percentage of Total Global PV Production

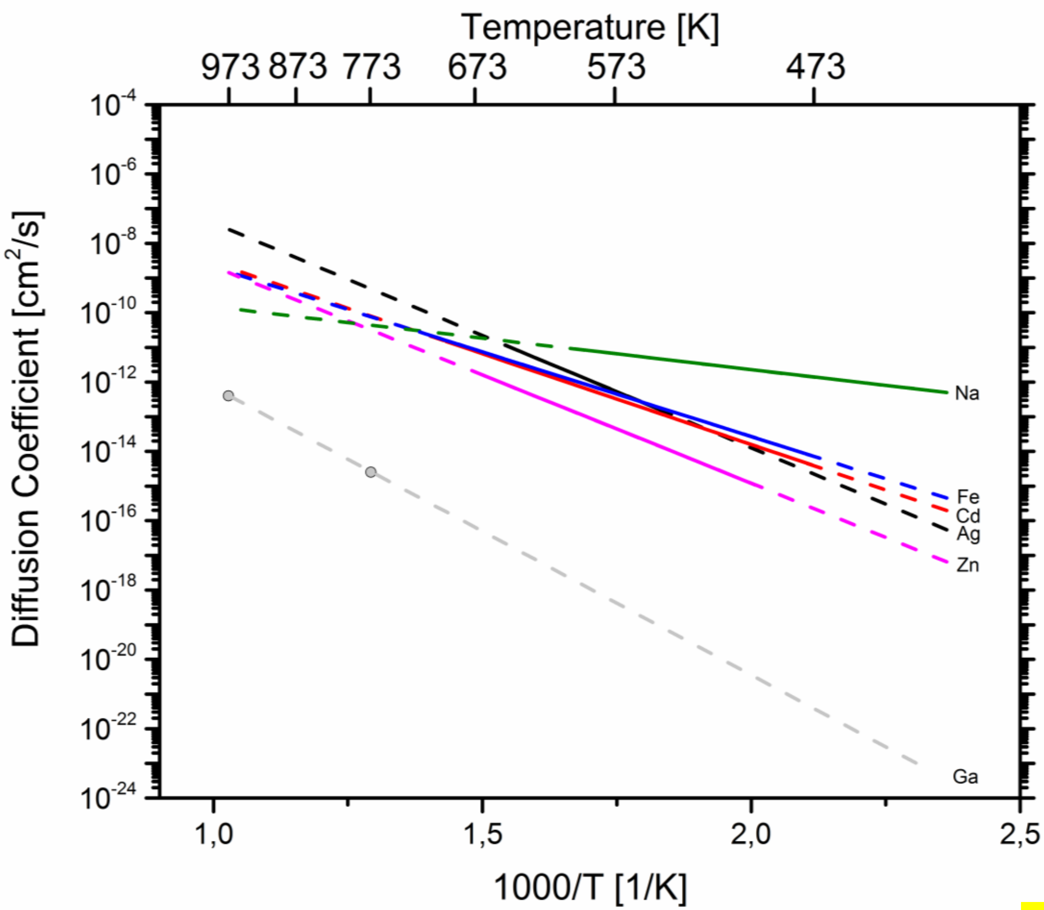


Data: from 2000 to 2010: Navigant; from 2011: IHS. Graph: PSE AG 2016

Fraunhofer ISE

Contamination of ^{67}Cu with ^{67}Ga (10-20%)

Master plot: diffusion in CIGS



^{67}Cu (β^-, ϒ) ^{67}Zn: 2.6 d

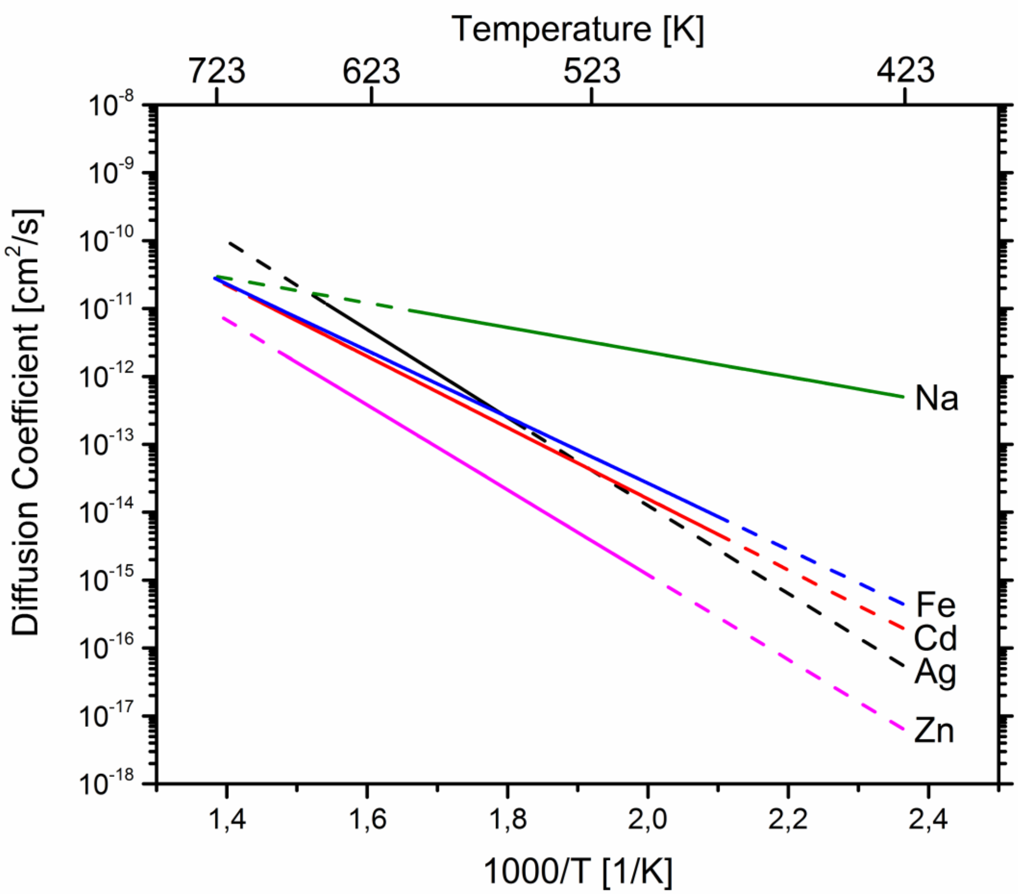
^{67}Ga (EC, ϒ)^{67}Zn: 3.3 d

No discrimination by ϒ or $t_{1/2}$

Expected: $D_{Cu} >> D_{Ga}$

Discrimination by diffusion depth !

Master Plot: Impurity Diffusion in CIGS



accommodated by Cu sublattice

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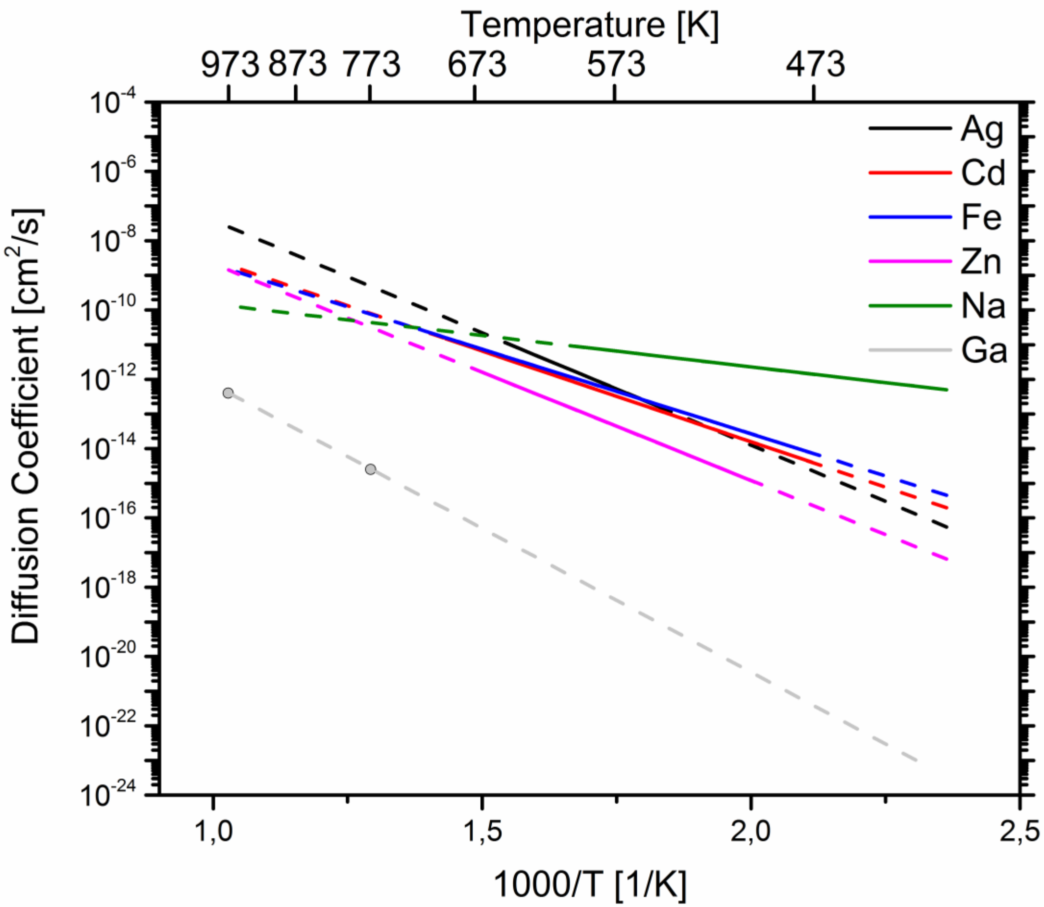

Temperature [K]
973
873
773
673
573
473
Diffusion Coefficient [cm^2/s]
10^{-4}
10^{-6}
10^{-8}
10^{-10}
10^{-12}
10^{-14}
10^{-16}
10^{-18}
10^{-20}
10^{-22}
10^{-24}
1,0
1,5
2,0
2,5
1000/T [1/K]
Ag
Cd
Fe
Zn
Na
Ga

Anion transference number : $t_{-} = \frac{D_{an^-}^{eff}}{D_{cat^+}^{eff} + D_{an^-}^{eff}} = \frac{D_{an^-}^{eff}}{D_{\sigma}}$

Fractional pair component : $f_{pair}^{an} = \frac{D_{pair}^{eff}}{D_{pair}^{eff} + D_{an^-}^{eff}} = \frac{D_{pair}^{eff}}{D_{an}^{*}}$

Meaning of Δ_{NE} : $\frac{1}{\Delta_{NE}} = \frac{1}{2}\left(\frac{1}{f_{pair}^{cat}} + \frac{1}{f_{pair}^{an}}\right)$

$$\sigma_{-} = t_{-}\sigma$$

$$t_{-} = 0.37$$

$$D_{Cu} >> D_{Fe}^{GB}$$

$$k_{PFG} = \gamma g^2 \delta^2 (\Delta - \delta / 3)$$

$$D_{Fe}^{V} > D_{Cu}^{V} > D_{Fe}^{GB}$$