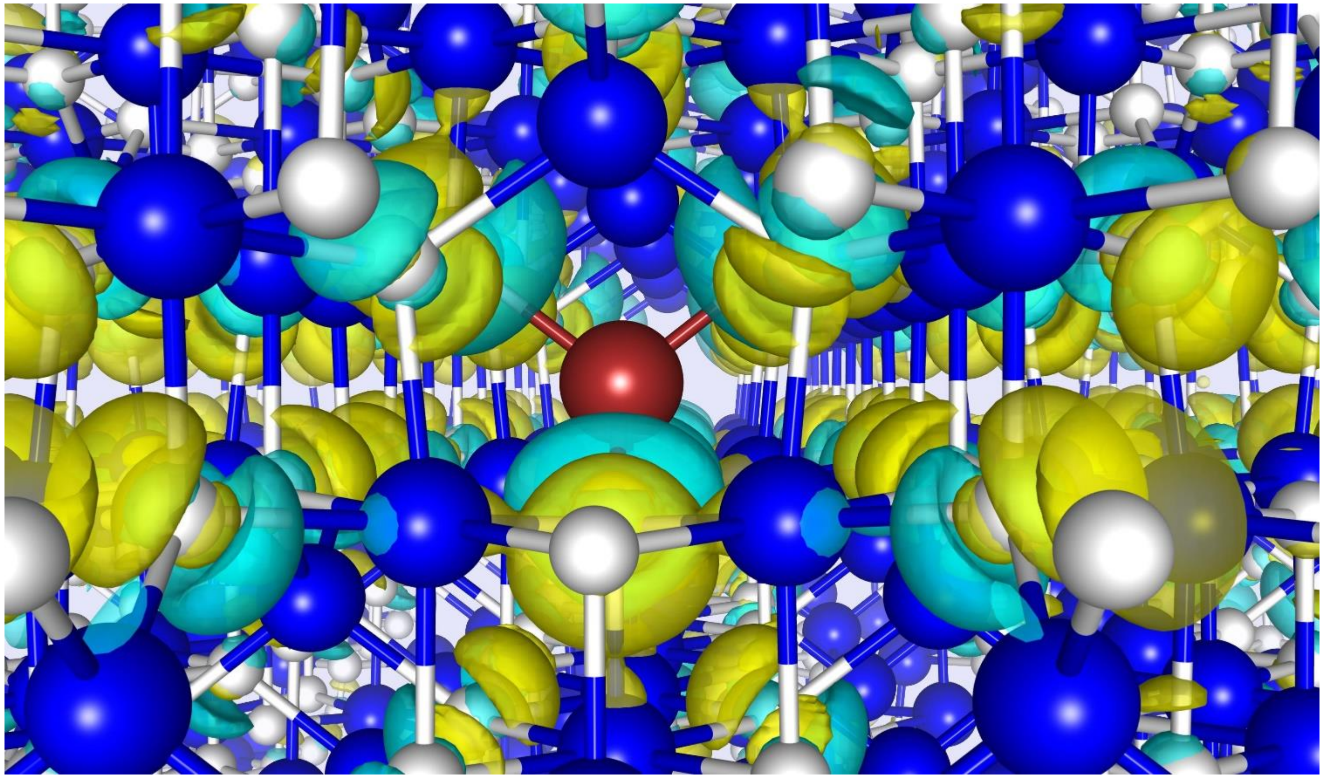
First-principles study of In_2S_3 as alternative buffer material for $Cu(In,Ga)(Se,S)_2$ thin-film solar cells



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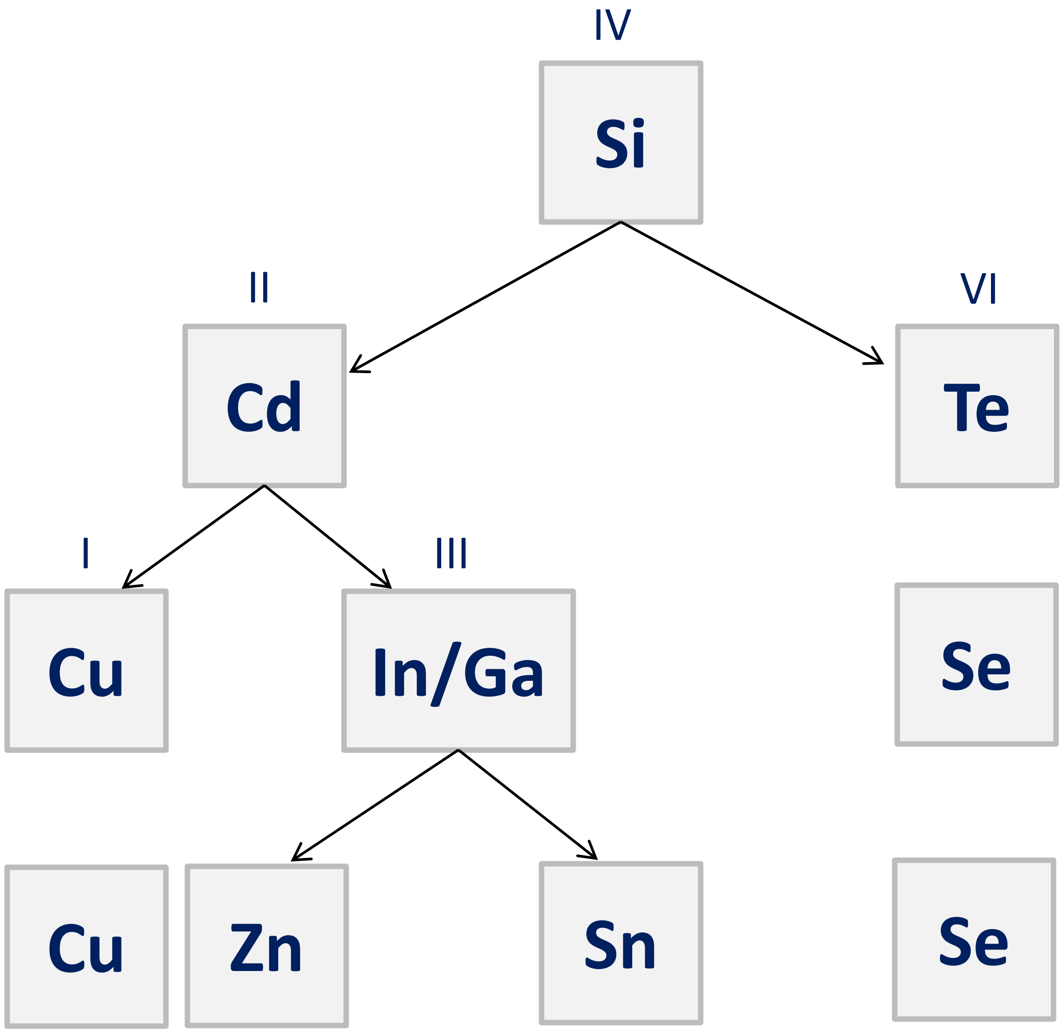
Fachgebiet Materialmodellierung
Darmstadt, Germany

Funded by BMWI-Project „Effcis“

Different types of solar cells



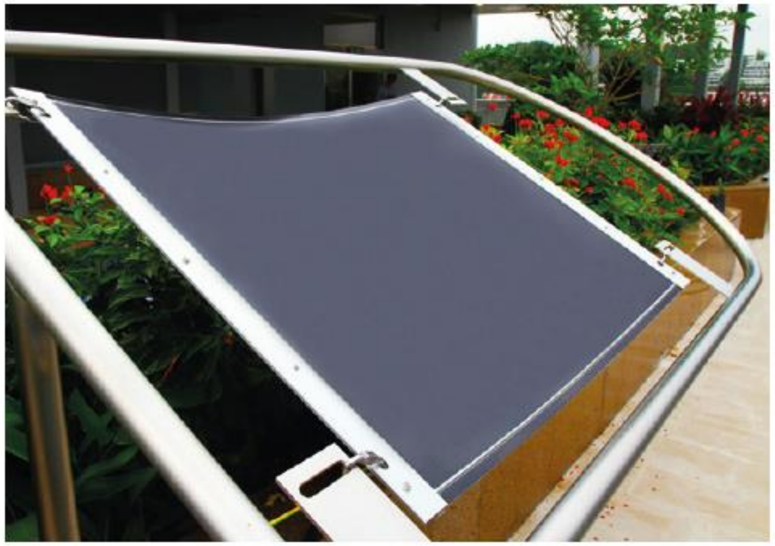
Si: Crystalline, non-toxic, high price, 24.1% efficiency

CdTe: Thin-film, involves toxic material, 21%efficiency

Cu(In,Ga)Se$_2$: Thin film, non-toxic, expensive elements, 23.4% efficiency

Cu$_2$(Zn,Sn)Se$_4$: Thin film, nontoxic, earth-abundant materials, 12.6% efficiency

CIGS-Modules



◀ *Monolithic CIGS on a flexible substrate, installed in Singapore.*

Flexible CIGS modules are lightweight and can be incorporated onto vehicle roofs and structures for which heavy PV modules are unsuitable. ▼

efficient

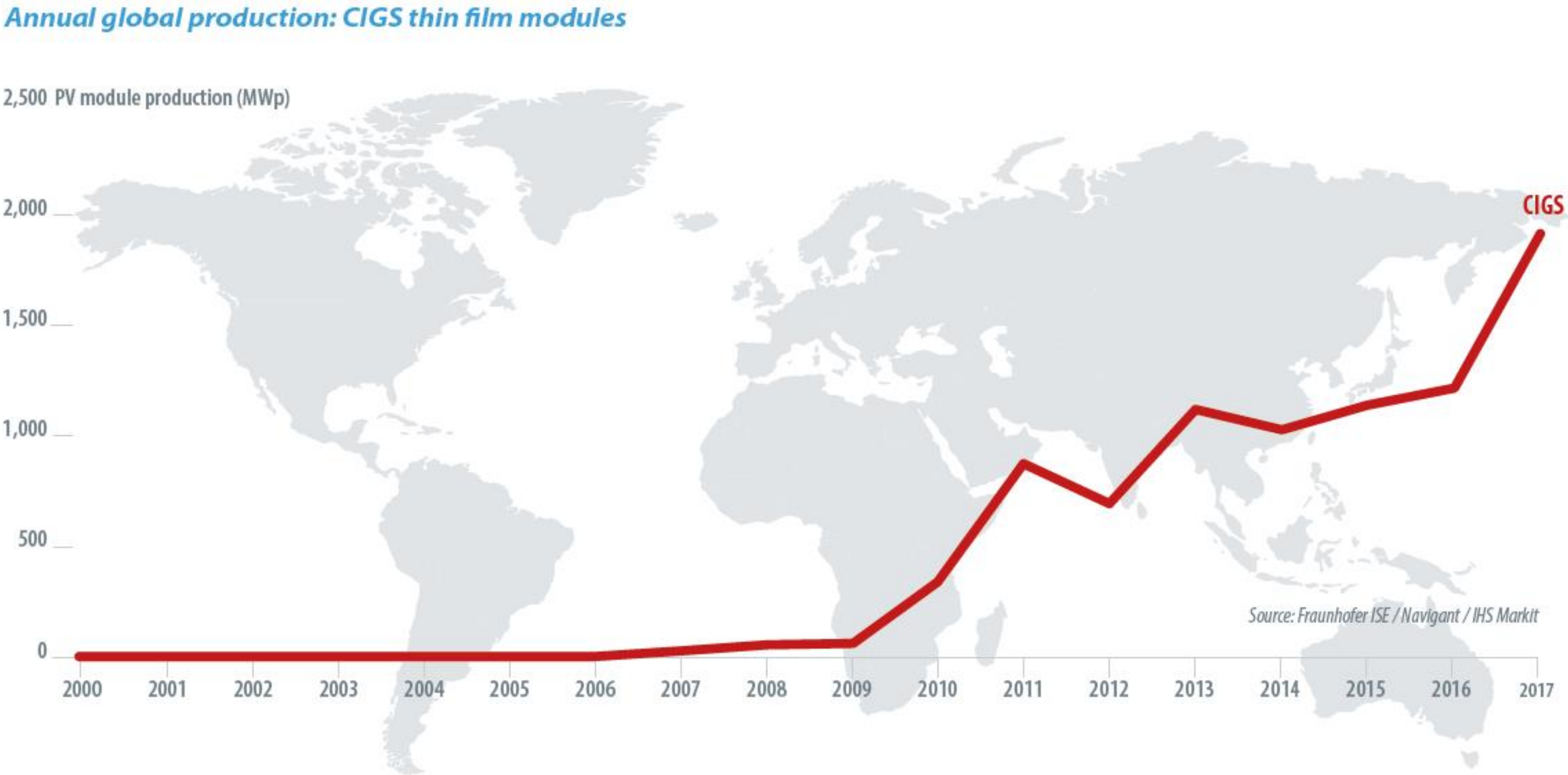
stable

beautiful

flexible

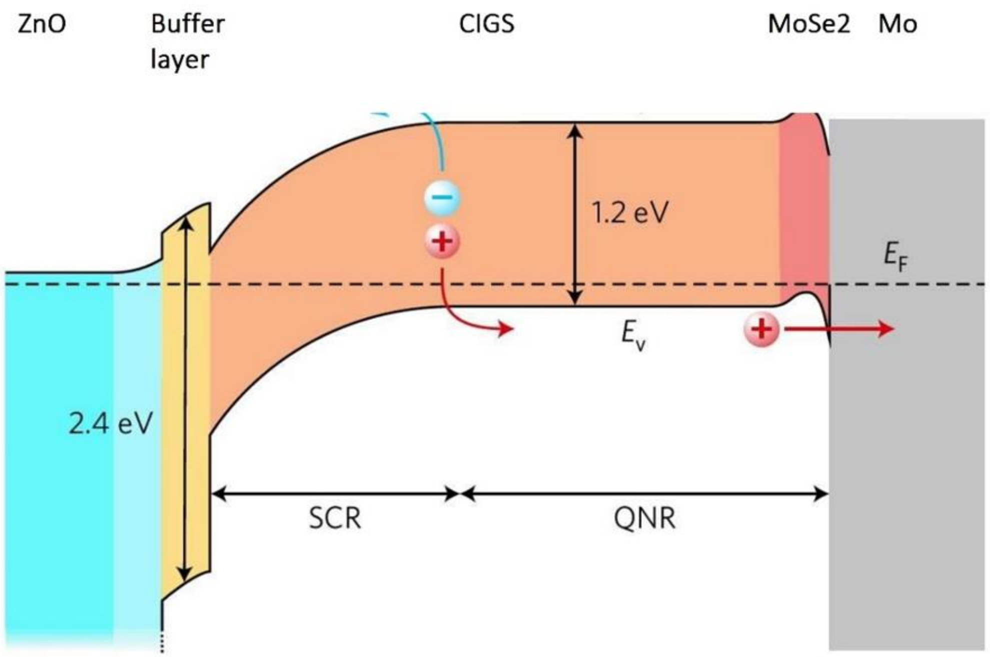
CIGS White Paper 2019

Annual global production of CIGS Modules



Source: Fraunhofer ISE / Navigant / IHS Markit

Role of buffer layer



- To form a junction with the absorber layer
- To admit a maximum amount of light to the junction region and absorber layer
- To drive out the photogenerated carries with minimum recombination losses to the outer circuit

In_2S_3 as buffer material

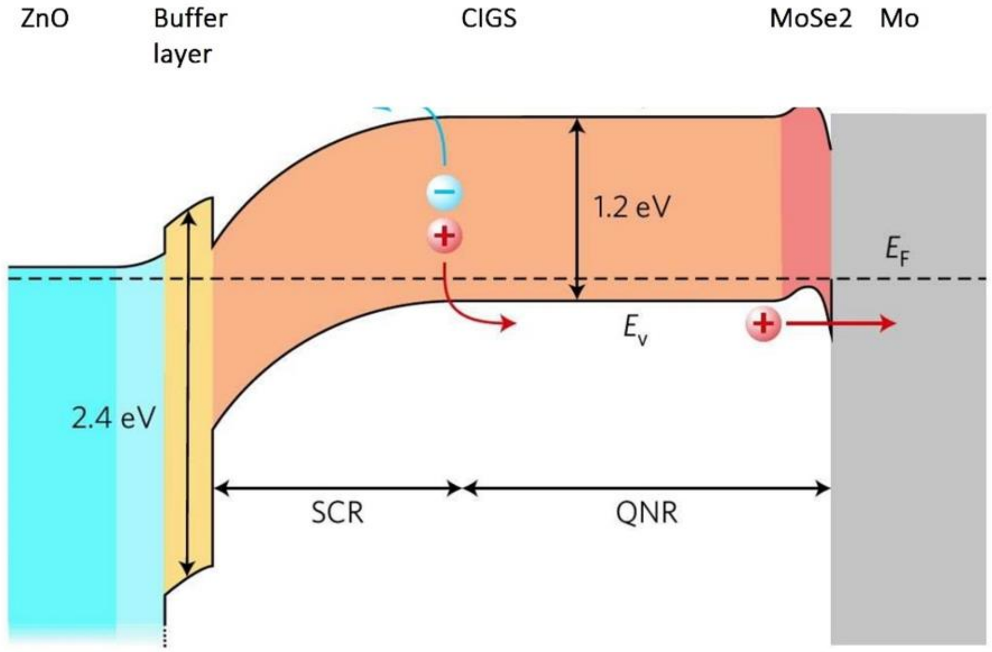
Why substituting CdS buffer layer?

- To avoid toxic metal-containing waste
- To avoid break in the production rate (chemical bath deposition technique)
- To increase QE in blue light region
- To reach higher efficiencies

Why In_xS_y as replacement?

- Enviromentally friendly
- It is compatible with various deposition methods
- Wider band gap when containing O, S or Na

CIGS-based solar cells with In_2S_3 buffer layer

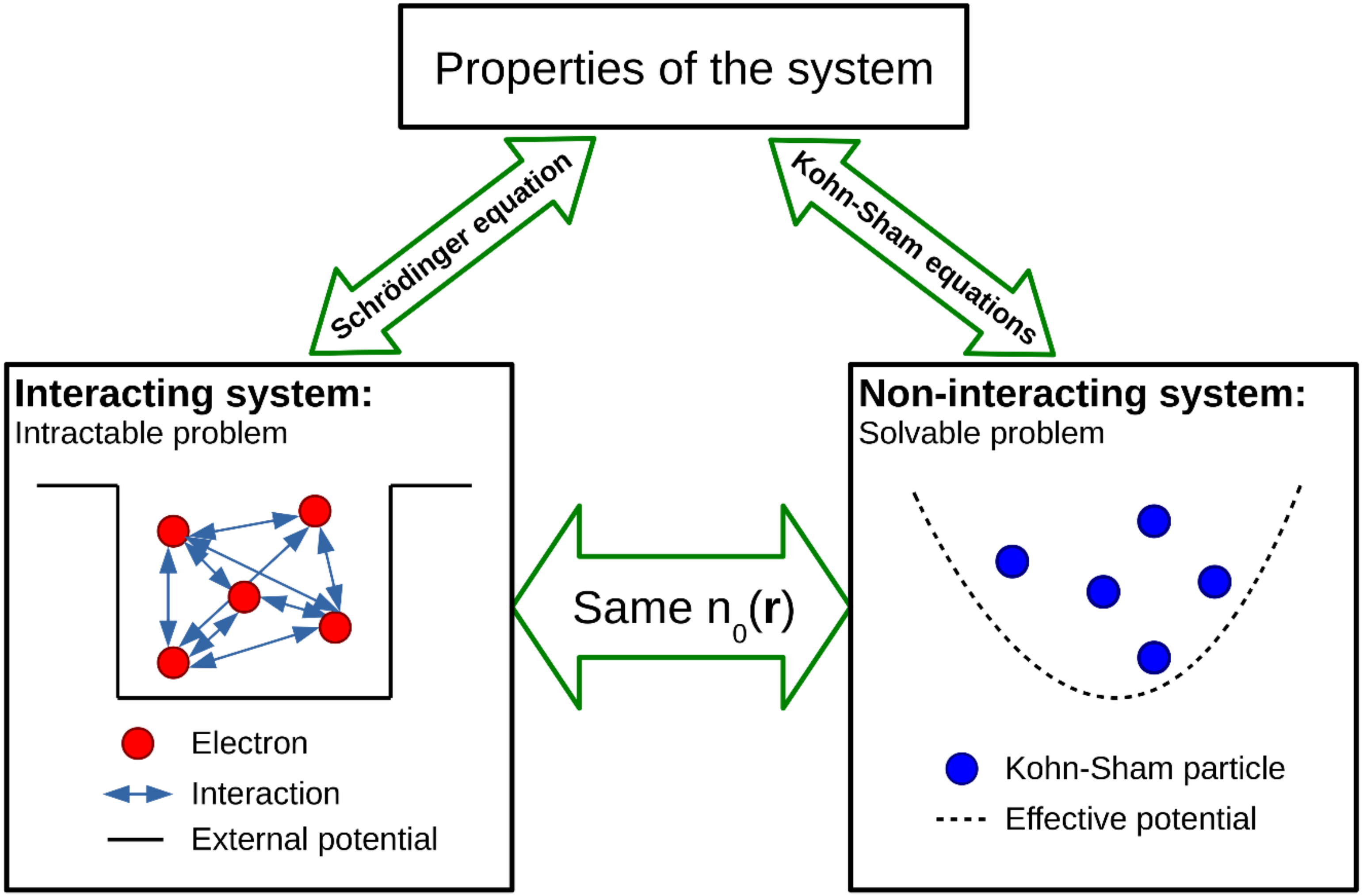


Is there a driving force for the formation of secondary phases at the interface?

Is the formation of secondary phases across the interface desirable or harmful?

Density Functional Theory (DFT)

P. Hohenberg and W. Kohn, Phys. Rev. B, **136**, B864-B871 (1964).
W. Kohn, L.J. Sham, Phys. Rev. **140**, 1133 (1965).



Properties of the system

Schrödinger equation

Kohn-Sham equations

Interacting system:
Intractable problem

● Electron
↔ Interaction
— External potential

Same $n_0(\mathbf{r})$

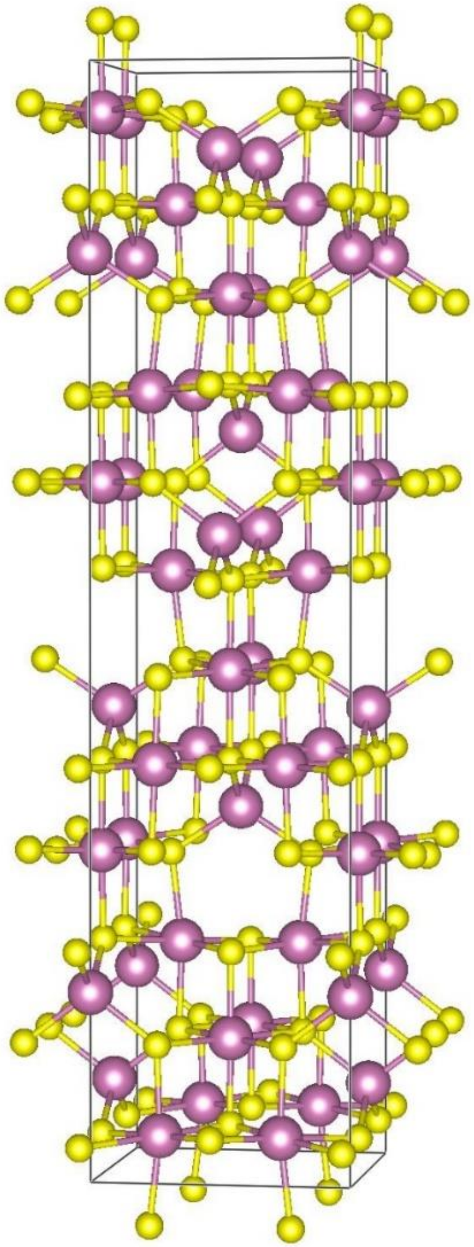
Non-interacting system:
Solvable problem

● Kohn-Sham particle
---- Effective potential

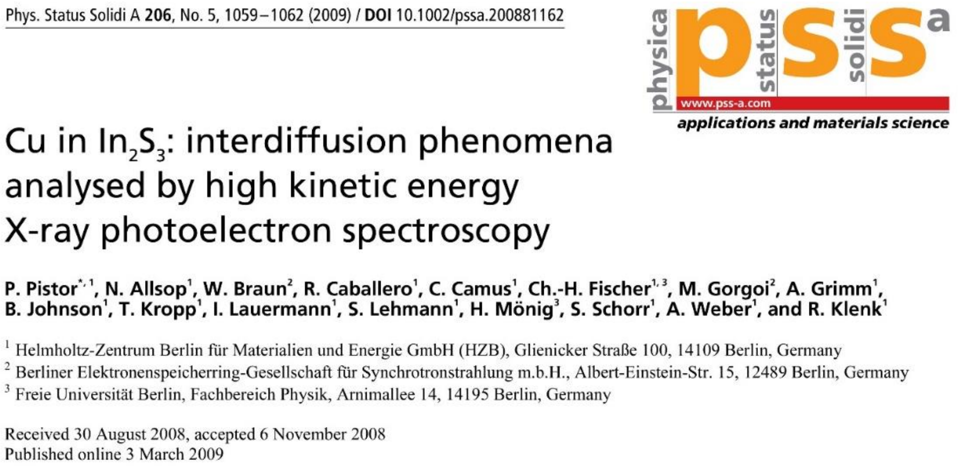
Calculated parameters for β-In_2S_3

	a (Å)	c/a	E_g (eV)	B (GPa)
This work	7.71	4.29	2.13	141
Exp.	7.62 [1]	4.26 [1]	2.1 - 2.4 [2,3]	148 [4]

[1] Rampersadh et al., *Physica B* (2004)
[2] Sterner et al., *Prog. Photovolt.: Res. Appl.* ***13*** (2005)
[3] Kitaiev et al., *Neorg. Mater.* ***12*** (1976)
[4] Amlouk et al., *Jpn. J. Appl. Phys.* ***38*** (1999)



CIGS/In_2S_3 interface: Literature review



Phys. Status Solidi A **206**, No. 5, 1059–1062 (2009) / **DOI** 10.1002/pssa.200881162

Cu in In_2S_3: interdiffusion phenomena analysed by high kinetic energy X-ray photoelectron spectroscopy

P. Pistor[*, 1], **N. Allsop**[1], **W. Braun**[2], **R. Caballero**[1], **C. Camus**[1], **Ch.-H. Fischer**[1, 3], **M. Gorgoi**[2], **A. Grimm**[1], **B. Johnson**[1], **T. Kropp**[1], **I. Lauermann**[1], **S. Lehmann**[1], **H. Mönig**[3], **S. Schorr**[1], **A. Weber**[1], **and R. Klenk**[1]

[1] Helmholtz-Zentrum Berlin für Materialien und Energie GmbH (HZB), Glienicker Straße 100, 14109 Berlin, Germany
[2] Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H., Albert-Einstein-Str. 15, 12489 Berlin, Germany
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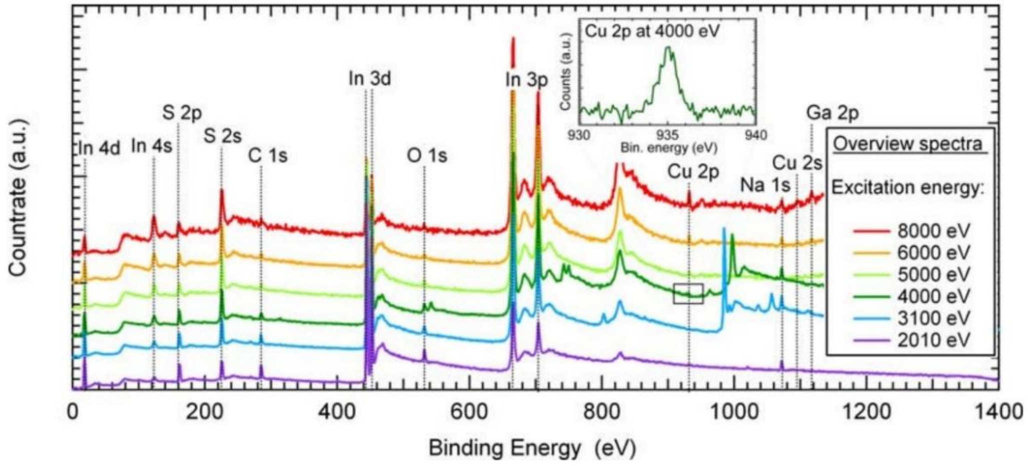

Progress in PHOTOVOLTAICS

PROGRESS IN PHOTOVOLTAICS: RESEARCH AND APPLICATIONS
Prog. Photovolt: Res. Appl. 2015; **23**:705–716
Published online 11 March 2014 in Wiley Online Library (wileyonlinelibrary.com). DOI: 10.1002/pip.2484

RESEARCH ARTICLE

Interface engineering and characterization at the atomic-scale of pure and mixed ion layer gas reaction buffer layers in chalcopyrite thin-film solar cells

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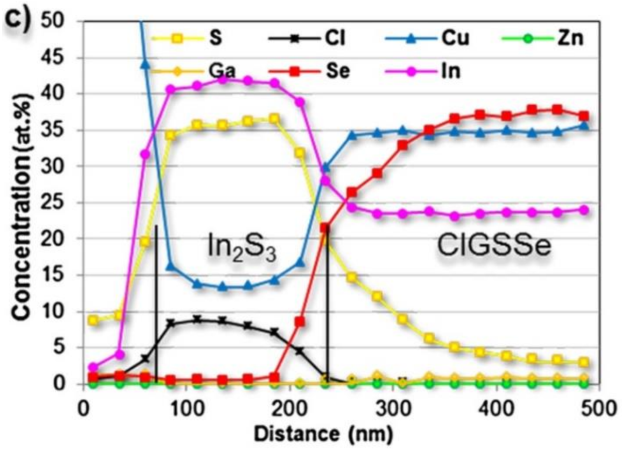
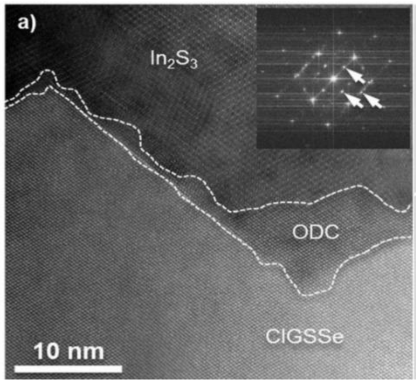




Thermodynamic modelling

Defect formation energy	$\Delta H = \Delta H_{\mathrm{D},q}\,(\boldsymbol{\mu},\boldsymbol{E}_\mathbf{F})$
Defect concentration	$c_\mathrm{D} \approx N_\mathrm{site} \times \exp(-\Delta H/kT)$
Electron/hole density	$c_e = \int f_\mathrm{FD}(E-\boldsymbol{E}_\mathbf{F})\, g(E)\,\mathrm{d}E$
Charge neutrality	$-\,c_e + c_h + \Sigma\,[q \cdot c(\mathrm{D}^q)] = 0$

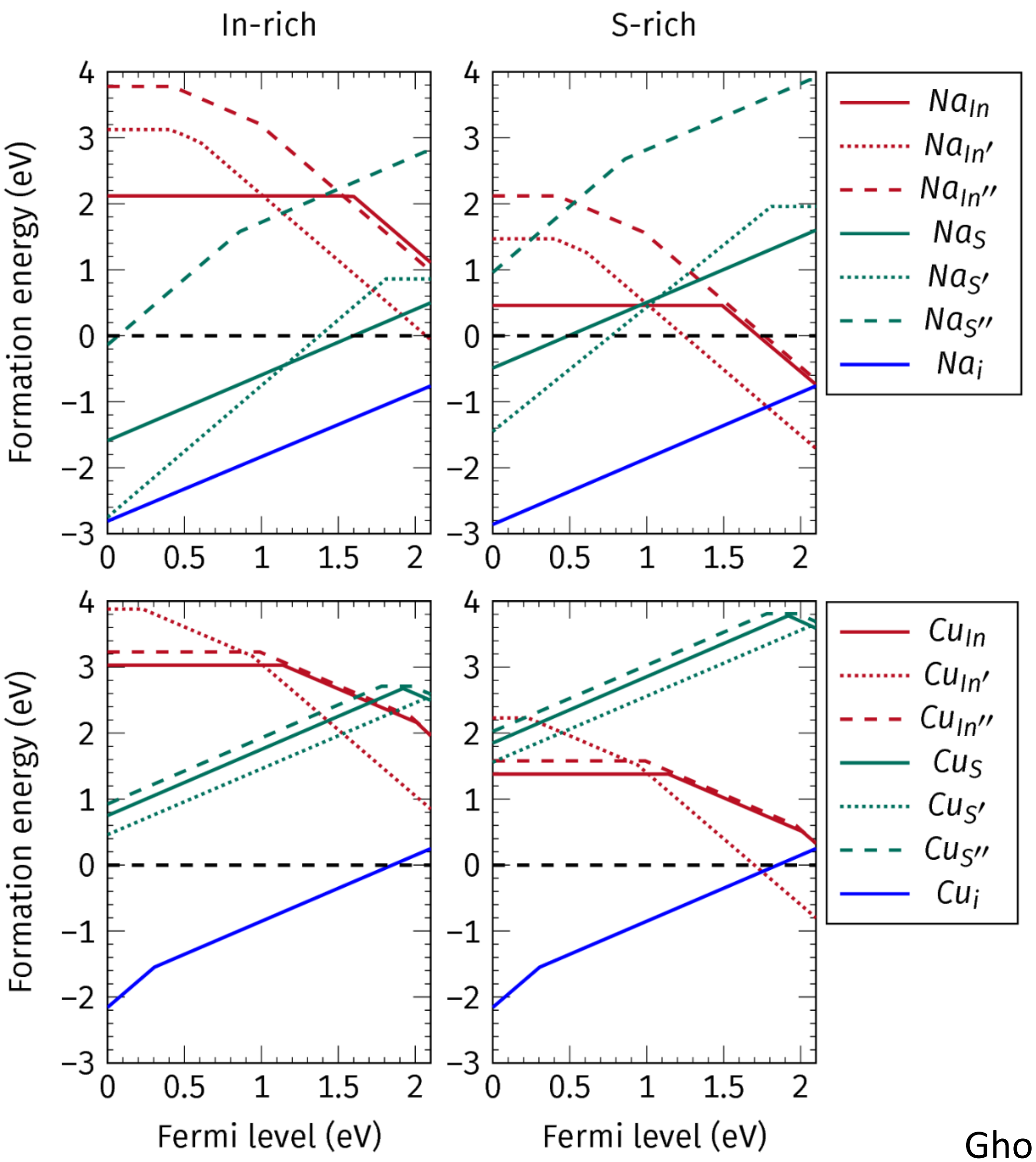
Self-consistent solution

$$\begin{tikzcd}
\Delta H(\boldsymbol{E}_\mathbf{F}) \arrow[r] & c_\mathrm{D}(\Delta H) \arrow[r] & \boldsymbol{E}_\mathbf{F} \arrow[ll, bend left]
\end{tikzcd}$$

$p\mathrm{O}_2$ dependence of μ_O	$\Delta\mu_\mathrm{O}(\boldsymbol{T},P_0) = \tfrac{1}{2}\,[H_0+\Delta H(\boldsymbol{T})] - \tfrac{1}{2}\boldsymbol{T}\cdot[S_0+\Delta S(\boldsymbol{T})]$
(ideal gas)	$\Delta\mu_\mathrm{O}(T,\boldsymbol{P}) = \Delta\mu_\mathrm{O}(T,\boldsymbol{P}_\mathbf{0}) + \tfrac{1}{2}kT\ln(\boldsymbol{P}/\boldsymbol{P}_\mathbf{0})$

High conc.	Account for competition of defects and host atoms for N_site Association/dissociation of ***defect-clusters*** (law of mass action)
Direct	Given $\Delta H(\mu)$, find concentrations c_D
Inverse	Given a target concentration, find ΔH (i.e., find μ)

Na and Cu in β-In_2S_3



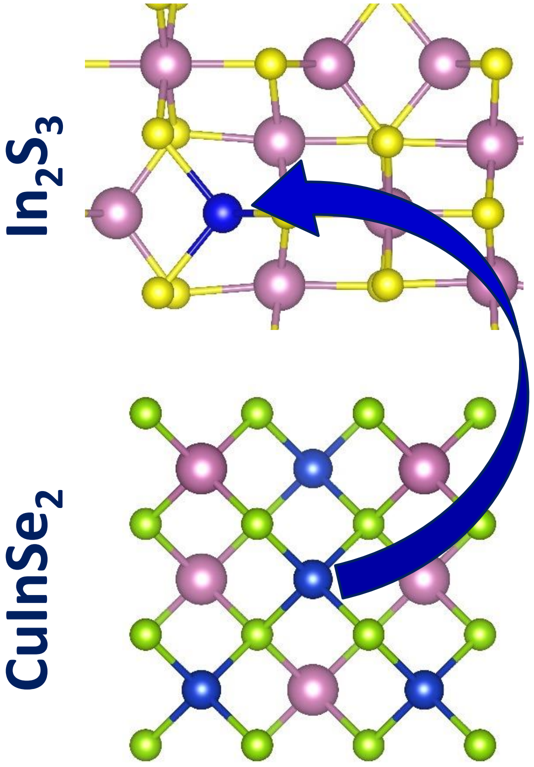
Ghorbani and Albe, *J. Mater. Chem. C* ***6*** (2018)

Na and Cu in β-In_2S_3

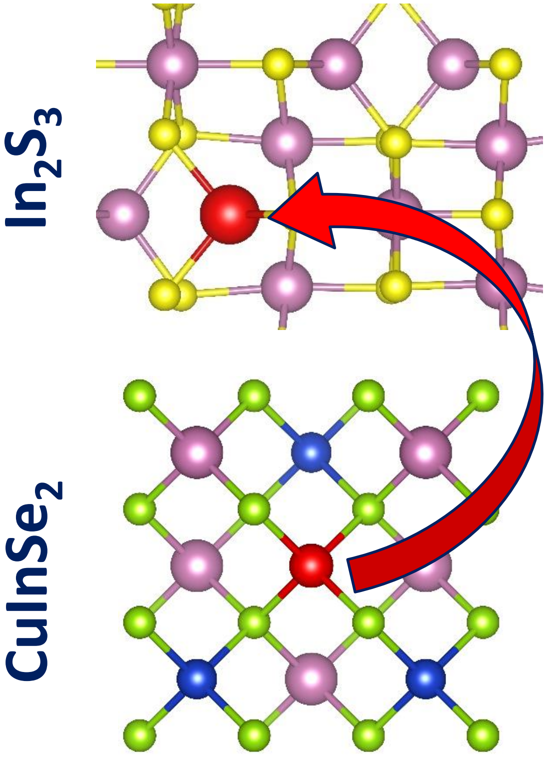
Is there a driving force for the transfer of Na and Cu into In_2S_3:

$$\text{Driving force} = \mathrm{E_{tot}(CIS\!:V_{Cu}) - E_{tot}(CIS\!:Na_{Cu}) + E_{tot}(In_2S_3\!:Na_i) - E_{tot}(In_2S_3\!:pure)}$$

$$\text{Driving force} = \mathrm{E_{tot}(CIS\!:V_{Cu}) - E_{tot}(CIS\!:pure) + E_{tot}(In_2S_3\!:Cu_i) - E_{tot}(In_2S_3\!:pure)}$$



$$\boldsymbol{DF(Cu) = -0.92\ eV}$$



$$\boldsymbol{DF(Na) = -1.51\ eV}$$

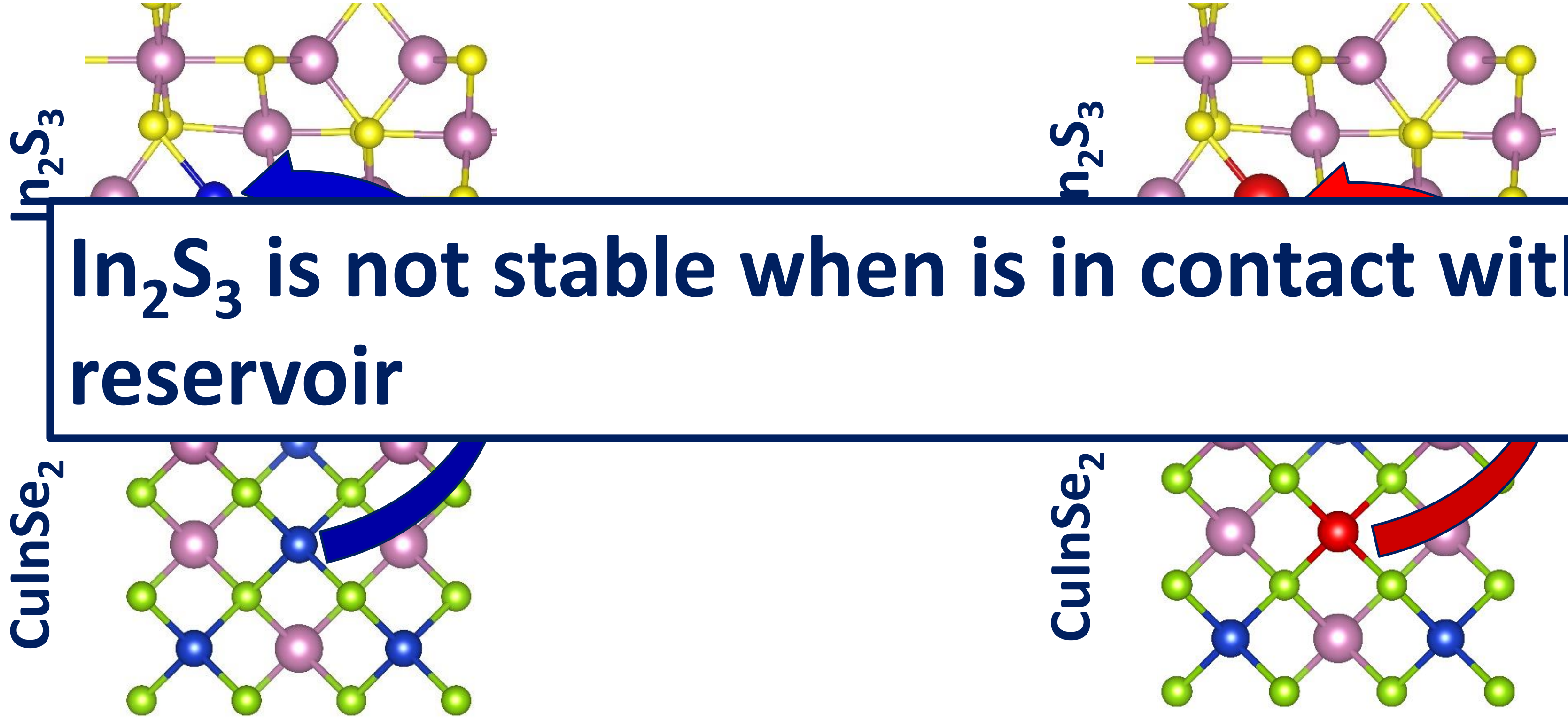
Ghorbani and Albe, *J. Mater. Chem. C* **6** (2018)

Na and Cu in β-In_2S_3

Is there a driving force for the transfer of Na and Cu into In_2S_3:

$$\text{Driving force} = E_{tot}(\text{CIS}: V_{Cu}) - E_{tot}(\text{CIS}: Na_{Cu}) + E_{tot}(In_2S_3: Na_i) - E_{tot}(In_2S_3: \text{pure})$$

$$\text{Driving force} = E_{tot}(\text{CIS}: V_{Cu}) - E_{tot}(\text{CIS}: \text{pure}) + E_{tot}(In_2S_3: Cu_i) - E_{tot}(In_2S_3: \text{pure})$$

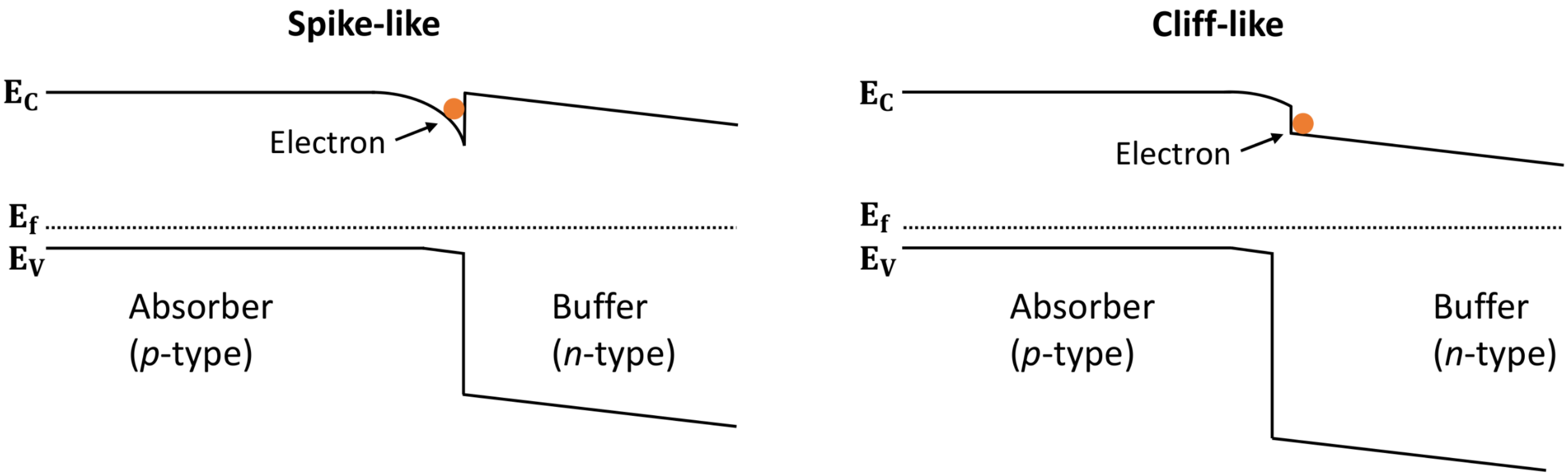


In_2S_3 is not stable when is in contact with Cu/Na reservoir

51 eV

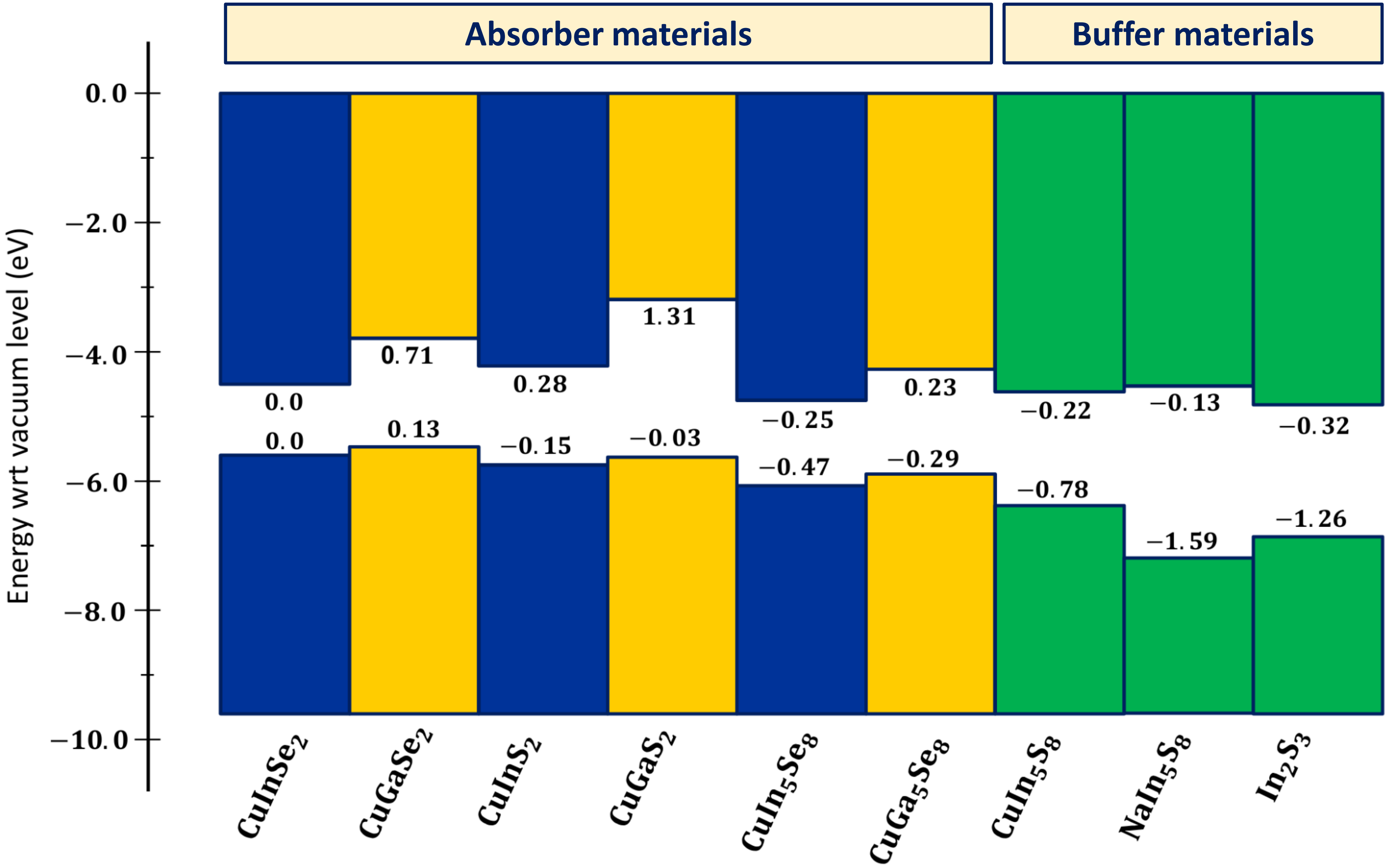
Ghorbani and Albe, *J. Mater. Chem. C* ***6*** (2018)

Absorber/buffer interface



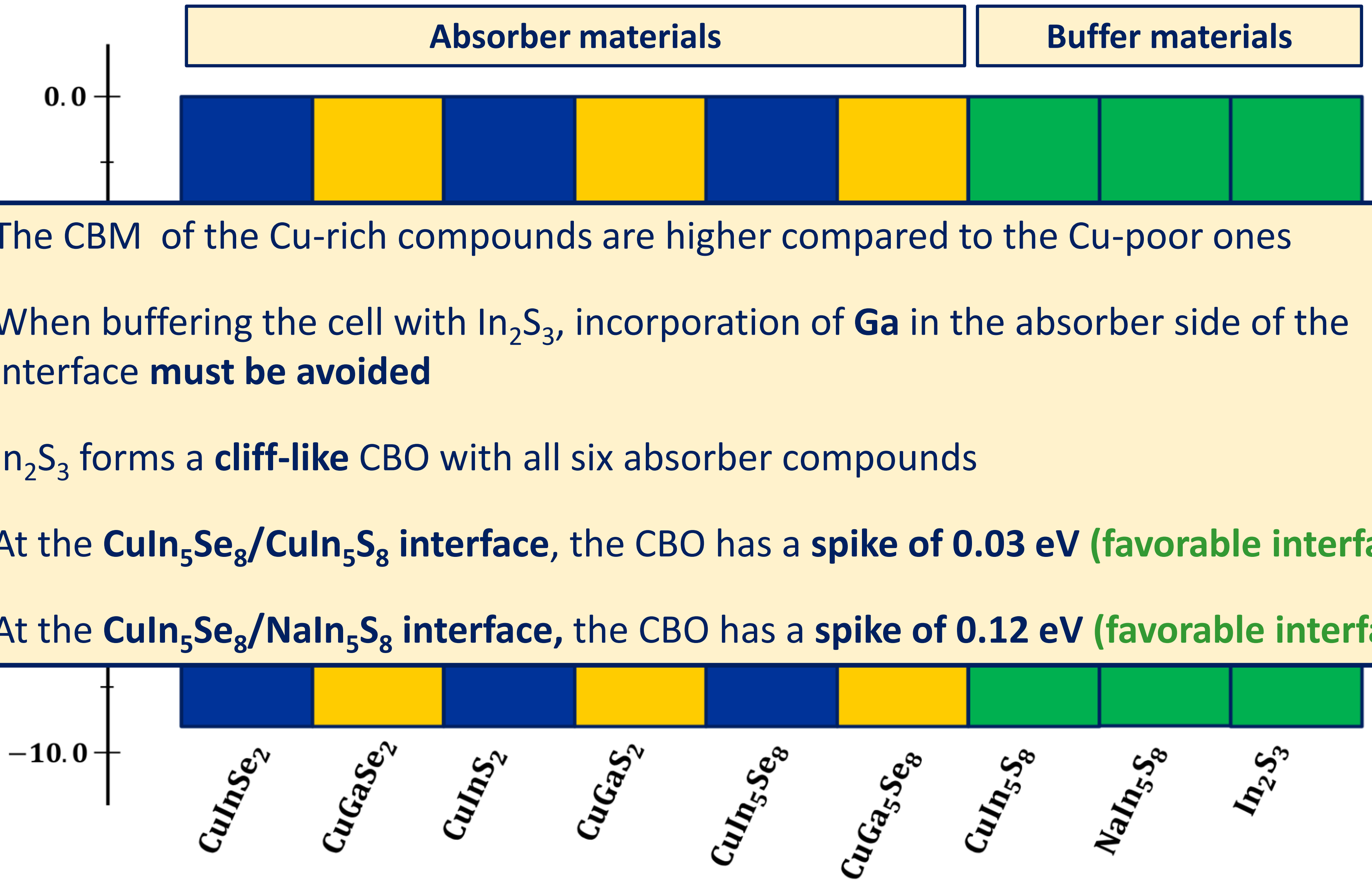
- A moderate spike-like offset (0.0-0.3 eV) suppresses charge recombination.
- A cliff-like offset triggers recombination and reduces the interface band gap.
- Cliff-like conduction band offset must be avoided.

Band alignment between ternary absorber compounds and In_2S_3



Ghorbani, Erhart and Albe, *Phys. Rev. Materials* **3** (2019)

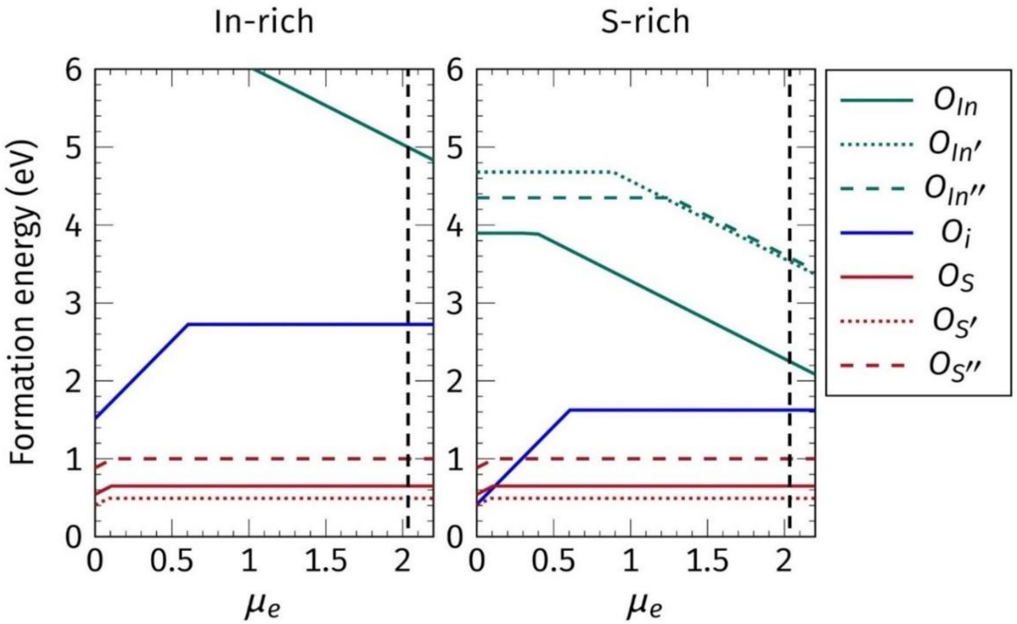
Band alignment between ternary absorber compounds and In_2S_3

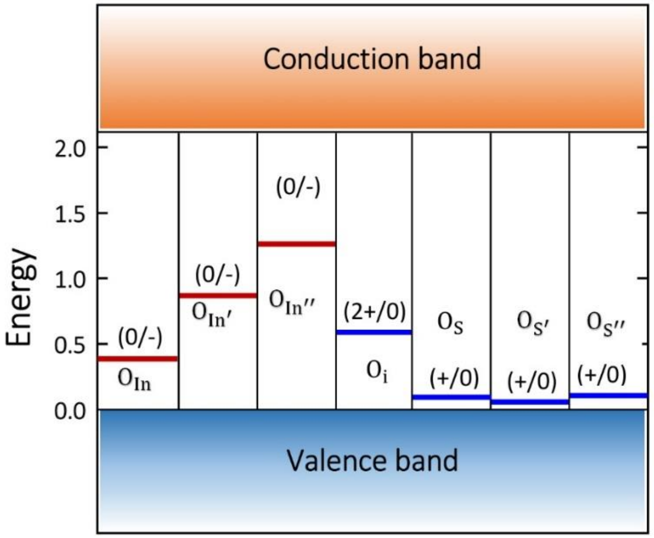


- The CBM of the Cu-rich compounds are higher compared to the Cu-poor ones
- When buffering the cell with In_2S_3, incorporation of **Ga** in the absorber side of the interface **must be avoided**
- In_2S_3 forms a **cliff-like** CBO with all six absorber compounds
- At the **$CuIn_5Se_8$/$CuIn_5S_8$ interface**, the CBO has a **spike of 0.03 eV** **(favorable interface)**
- At the **$CuIn_5Se_8$/$NaIn_5S_8$ interface,** the CBO has a **spike of 0.12 eV** **(favorable interface)**

Ghorbani, Erhart and Albe, *Phys. Rev. Materials* **3** (2019)

Oxygen in β-In_2S_3

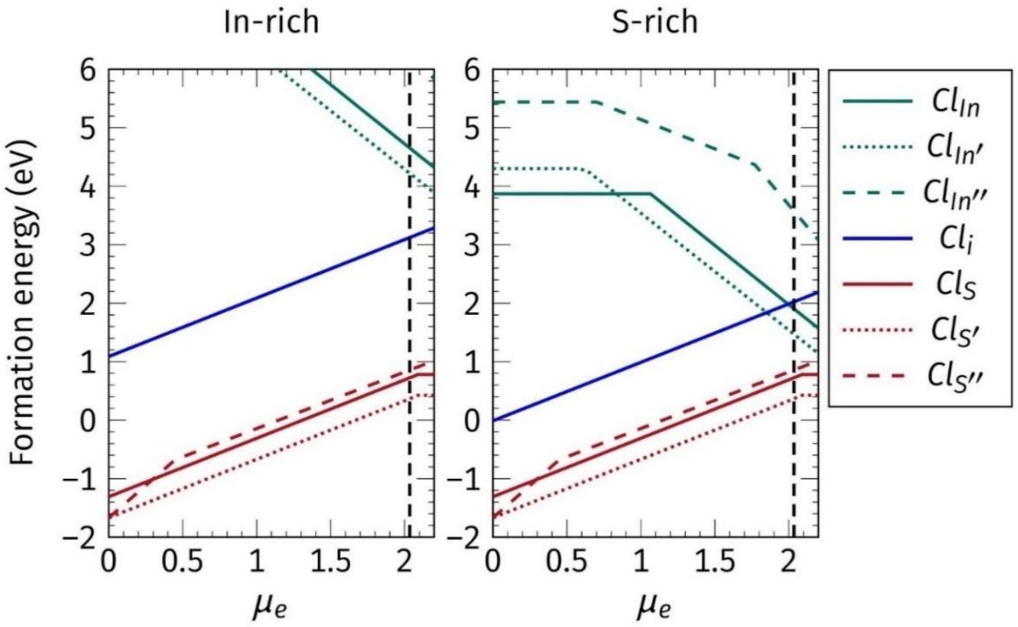


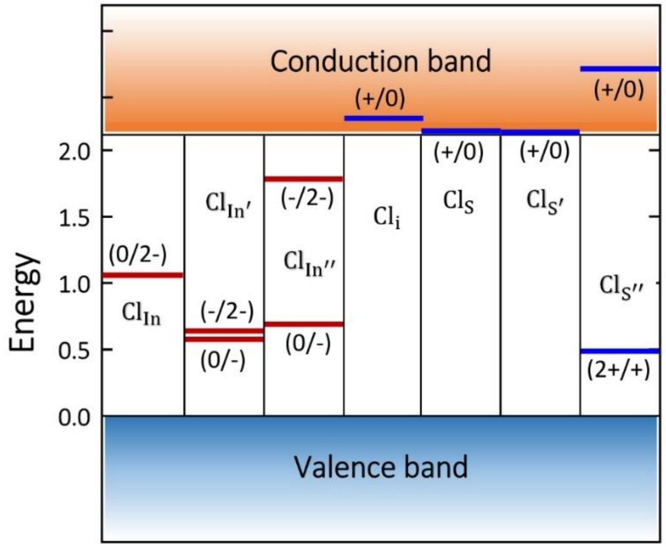


- β-In_2S_3 is an stable material when subjected to oxygen reservoir.
- For both In- and S-rich samples, formation energies of oxygen in different sulfur sites is low, which indicates that O substituting anionic site forms in indium sulfide in ample concentrations.
- Oxygens in all sulfur sites induce an extremely deep (0/+) donor level close to VBM – Being electrically inactive.

Ghorbani and Albe, *Phys. Rev. B* **98** (2018)

Chlorine in β-In_2S_3





- β-In_2S_3 is an stable material when subjected to chlorine reservoir.
- Concentration of Cl on sulfur lattice sites is large.
- Incorporation of Cl-on-In sites under In-rich condition are very high in energy, hence, their formation is improbable. However, under S-rich condition their formation becomes probable.
- Incorporation of Cl in all sulfur sites features a **raise in n-type conductivity**.

Ghorbani and Albe, *Phys. Rev. B* **98** (2018)

Take-home message

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DARMSTADT

I. Na and Cu in β-In_2S_3

- Independent of the $CuInSe_2/In_2S_3$ interface orientation, having a stable interface in the presence of Na and Cu reservoir is thermodynamically impossible

II. Band alignemnt at the absorber/buffer interface

- In_2S_3 forms an unfavorable cliff-like CBO with all CIGS absorber compounds
- At the $CuIn_5Se_8/CuIn_5S_8$ interface, the CBO has a spike of 0.03 eV
- At the $CuIn_5Se_8/NaIn_5S_8$ interface, the CBO has a spike of 0.12 eV

III. O and Cl in β-In_2S_3

- Despite Cu and Na, O and Cl in the buffer side of the interface present in lower concentrations, and do not trigger chemical modification of the In_2S_3
- O_i and Cl_{In} are the sources of n-type PPC in doped In_2S_3
- There is a large miscibility gap between In_2S_3 and In_2O_3