

Intrinsic *DX* centers in ternary chalcopyrite semiconductors

“Why metastable intrinsic defects cause open-circuit-voltage limitation and how they can be avoided”

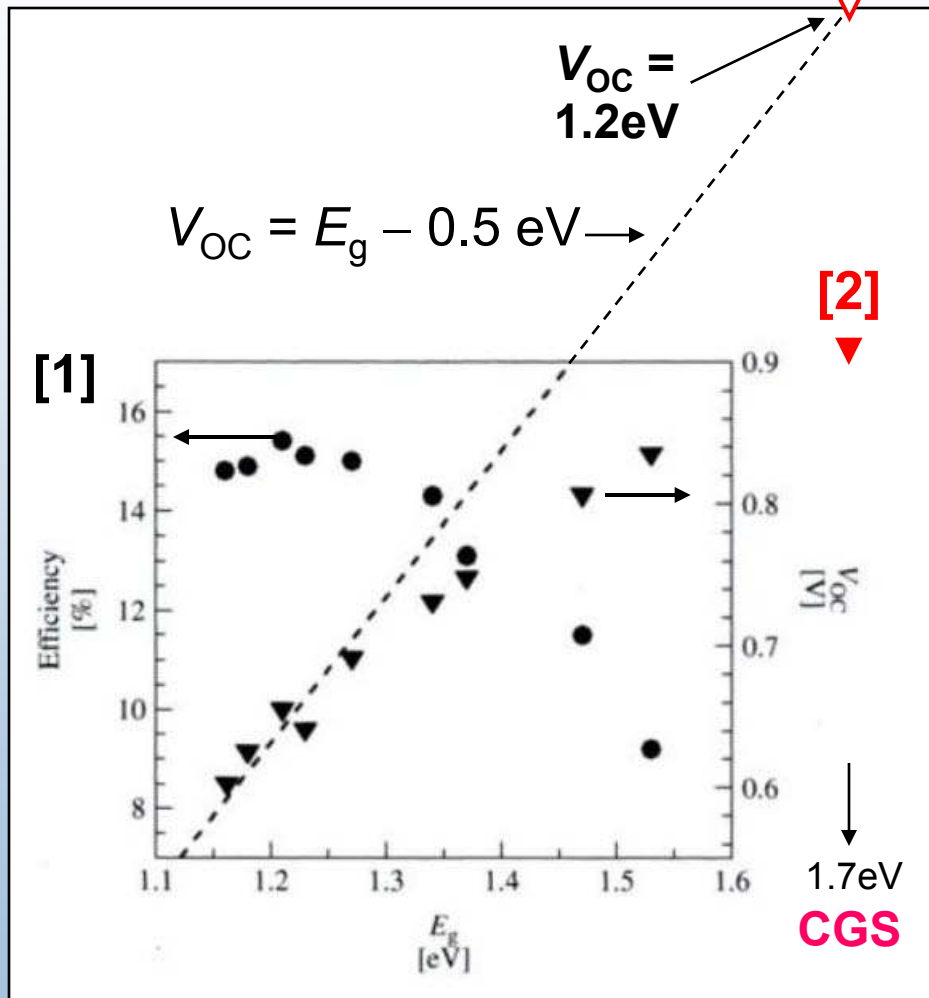
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V_{OC} saturation in CIGS

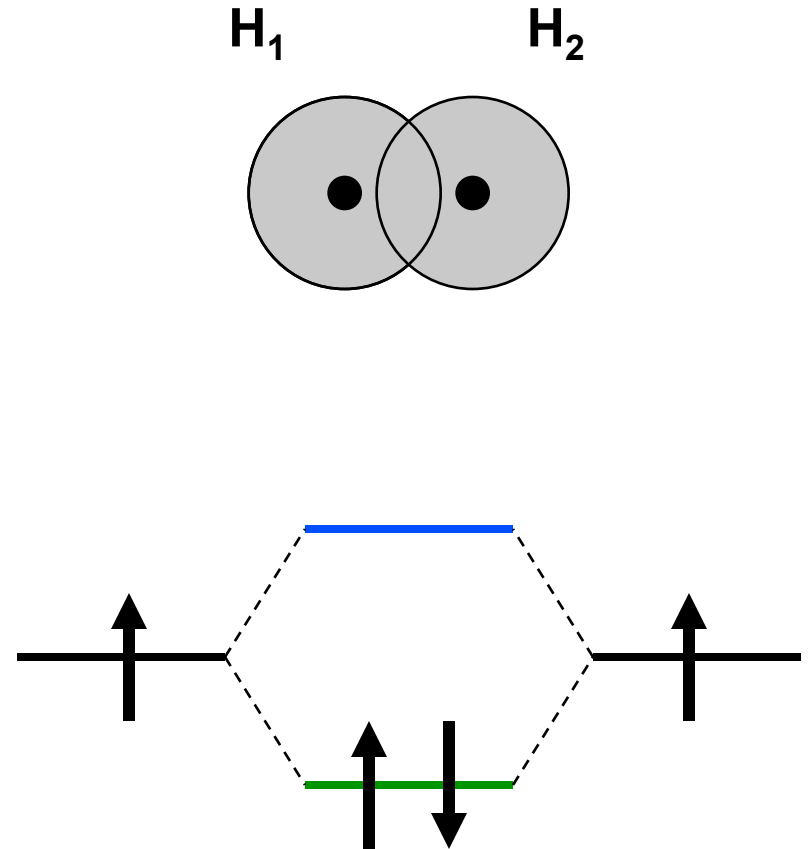
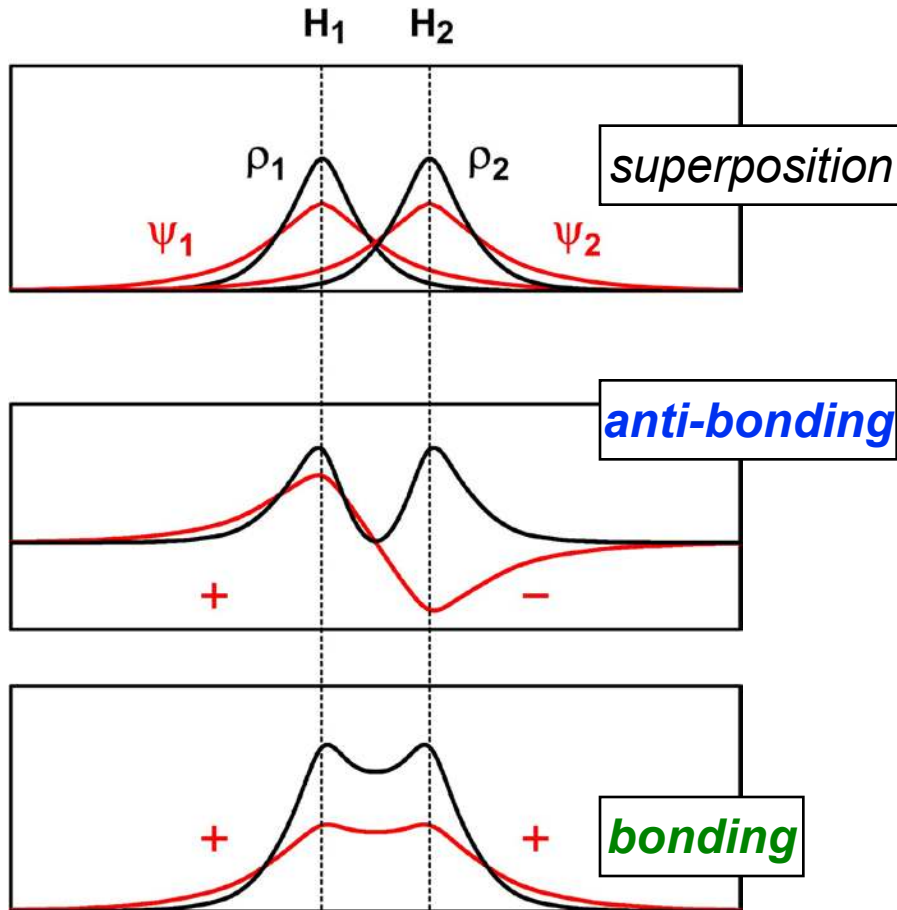


Higher V_{OC} :

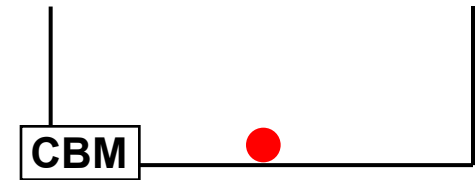
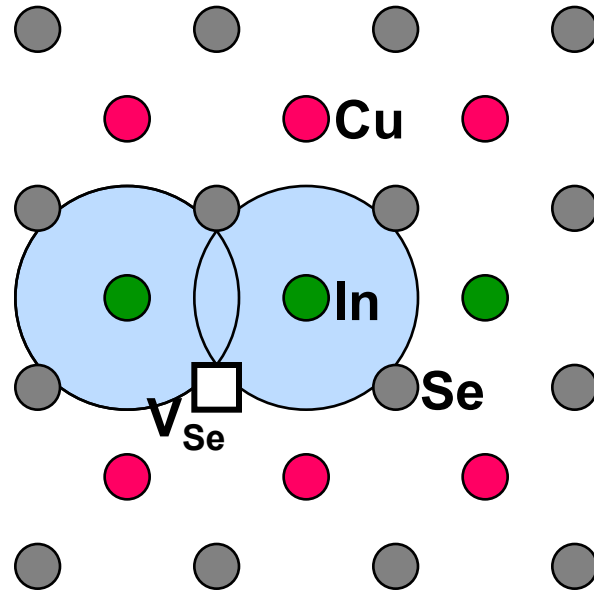
- Higher η for single-junction
- Needed for TF tandem
- Reason: Recombination due to deep defects [3]

- [1] W.N. Shafarman and L. Stolt, in: *Handbook of Photovoltaic Science and Engineering*
- [2] R. Kniese, M. Lammer, U. Rau, M. Powalla, TSF **451-452**, 430 (2004).
- [3] G. Hanna, A. Jasenek, U. Rau, H.W. Schock, TSF **387**, 71 (2001).

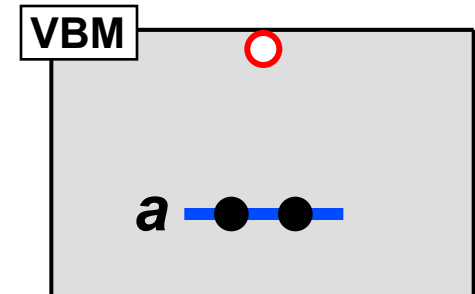
Defects levels (I) – Example: Orbital interaction in the H₂ molecule



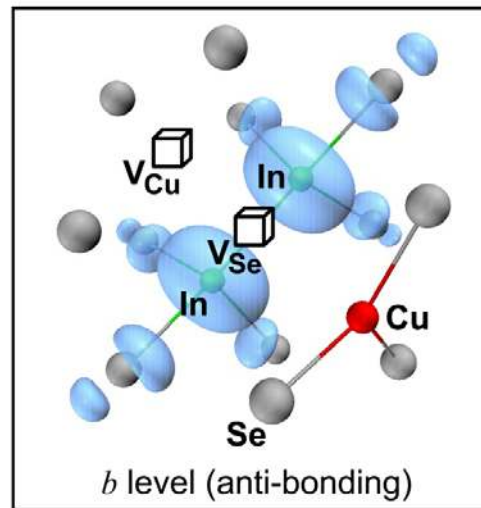
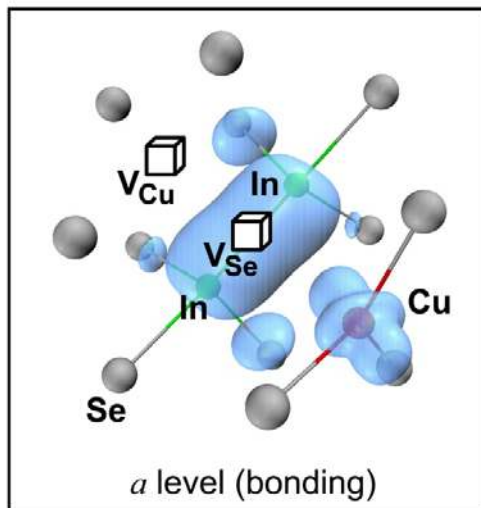
Defects levels (II): Se-vacancy in CuInSe_2



b ———

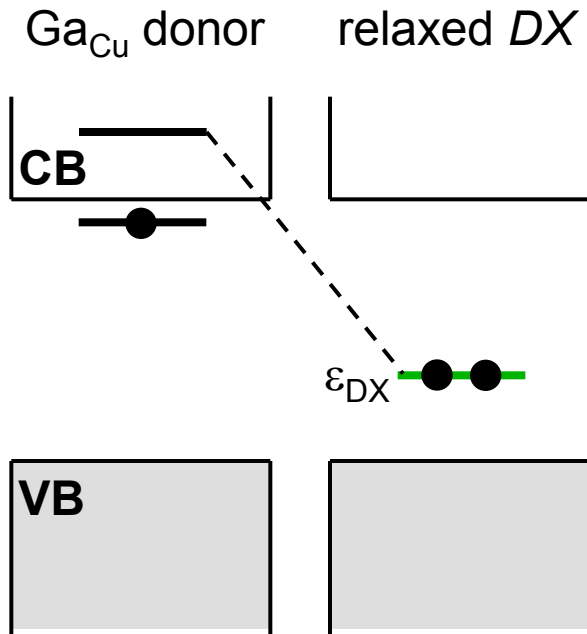


a —●—●—

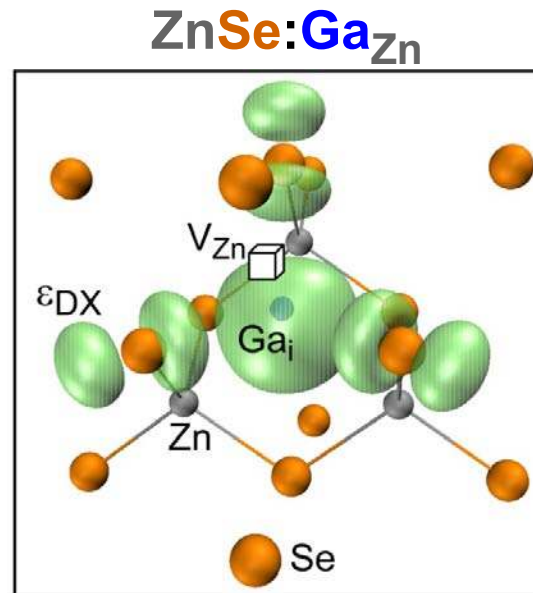


***Intrinsic DX* centers in ClGS**

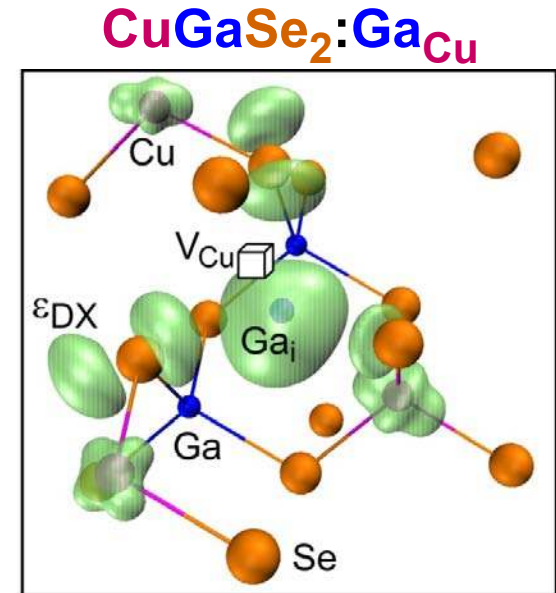
DX centers: *Electron traps formed due to lattice relaxations*



Extrinsic DX in II-VI

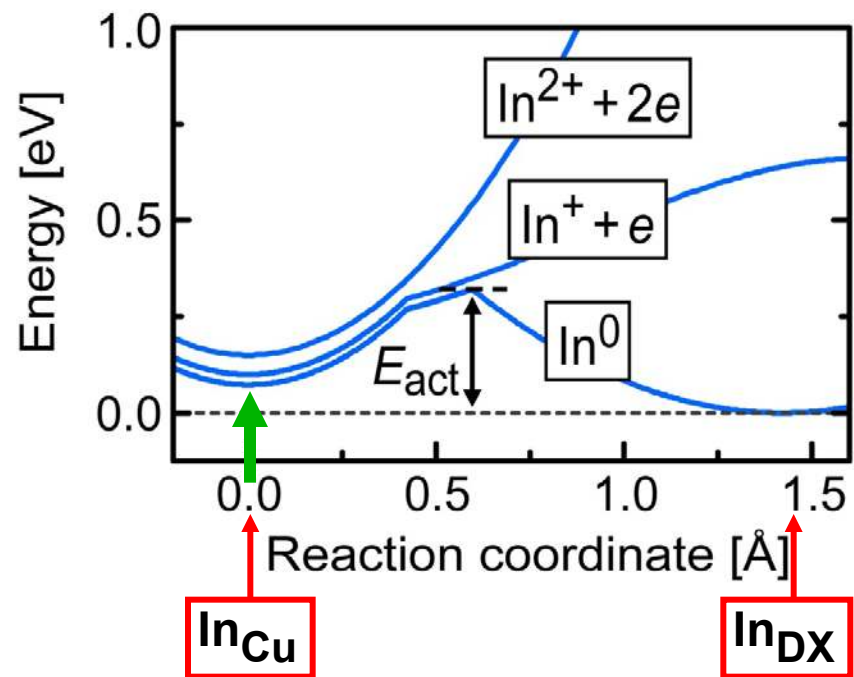
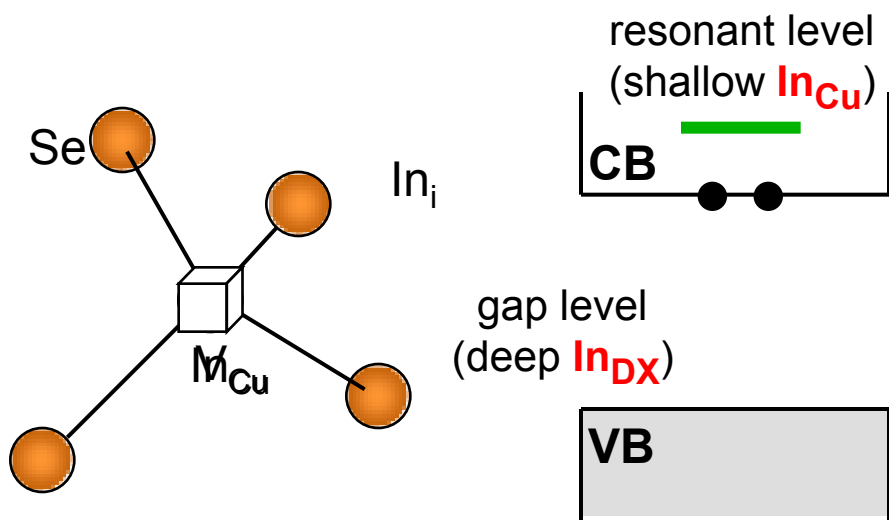


Intrinsic DX in CIGS



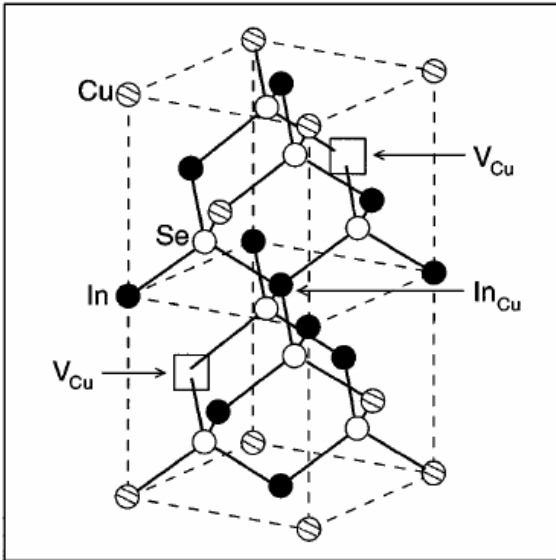
In II-VI, DX centers require **extrinsic** impurities
In CIGS, **native defects** (In_{Cu}, Ga_{Cu}) exhibit DX behavior

Evolution of ionic structure, electron-level, and energy during the transition into the deep DX state



Critical Fermi levels for electron-trapping

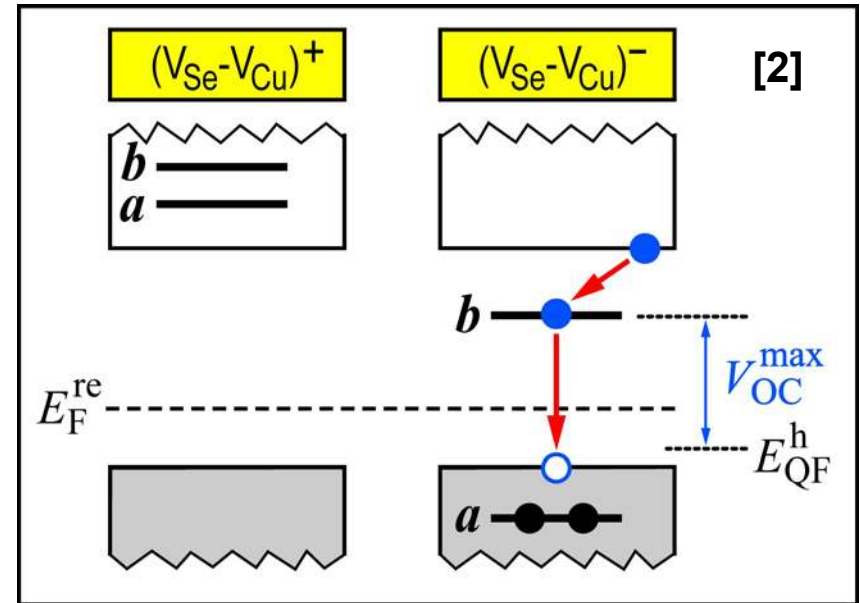
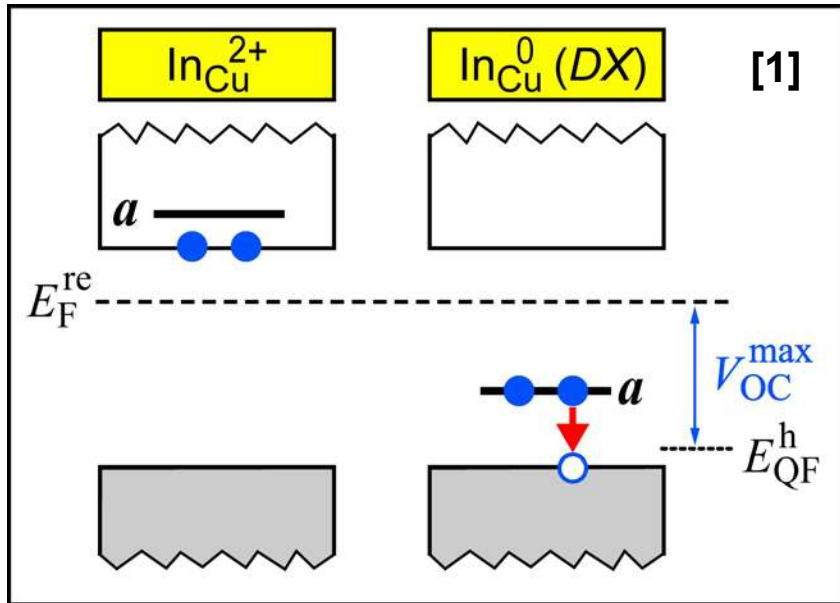
In_{Cu} (Ga_{Cu}) exists isolated or in complexes, e.g., $(\text{In}_{\text{Cu}}-2\text{V}_{\text{Cu}})$ [1]



Transition		occurs above $E_{\text{F}} > E_{\text{V}} +$
$\text{In}_{\text{Cu}}^{2+}$	$+ 2e \rightarrow \text{In}_{\text{DX}}^0$	0.9 eV
$(\text{In}_{\text{Cu}}-\text{V}_{\text{Cu}})^+$	$+ 2e \rightarrow (\text{In}_{\text{DX}}-\text{V}_{\text{Cu}})^-$	1.1 eV
$(\text{In}_{\text{Cu}}-2\text{V}_{\text{Cu}})^0$	$+ 2e \rightarrow (\text{In}_{\text{DX}}-\text{V}_{\text{Cu}})^{2-}$	1.3 eV

Electron-trapping due to DX centers occurs mainly in wider-gap $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ alloys with $x \geq 0.3$

V_{OC} limitation by In_{Cu} , Ga_{Cu} , V_{Se} and their complexes with V_{Cu}



In_{Cu} , Ga_{Cu} : V_{OC} is limited by the transition that causes atomic reconfiguration
 $V_{Se}-V_{Cu}$: The negative (acceptor) configuration exhibits deep trap level
 Both types of defects limit V_{OC} below ~ 1 eV

[1] S. Lany and A. Zunger, Phys. Rev. Lett. **100**, 016401 (2008).

[2] S. Lany and A. Zunger, J. Appl. Phys. **100**, 113725 (2006).

***How to avoid V_{OC} limiting
metastable defects?***

Formation energies vs growth conditions

$$\Delta H_{D,q}(\mu, E_F) = [E_{D,q} - E_{\text{host}}] + [\mu_{\text{host}} - \mu_D] + q \cdot E_F$$

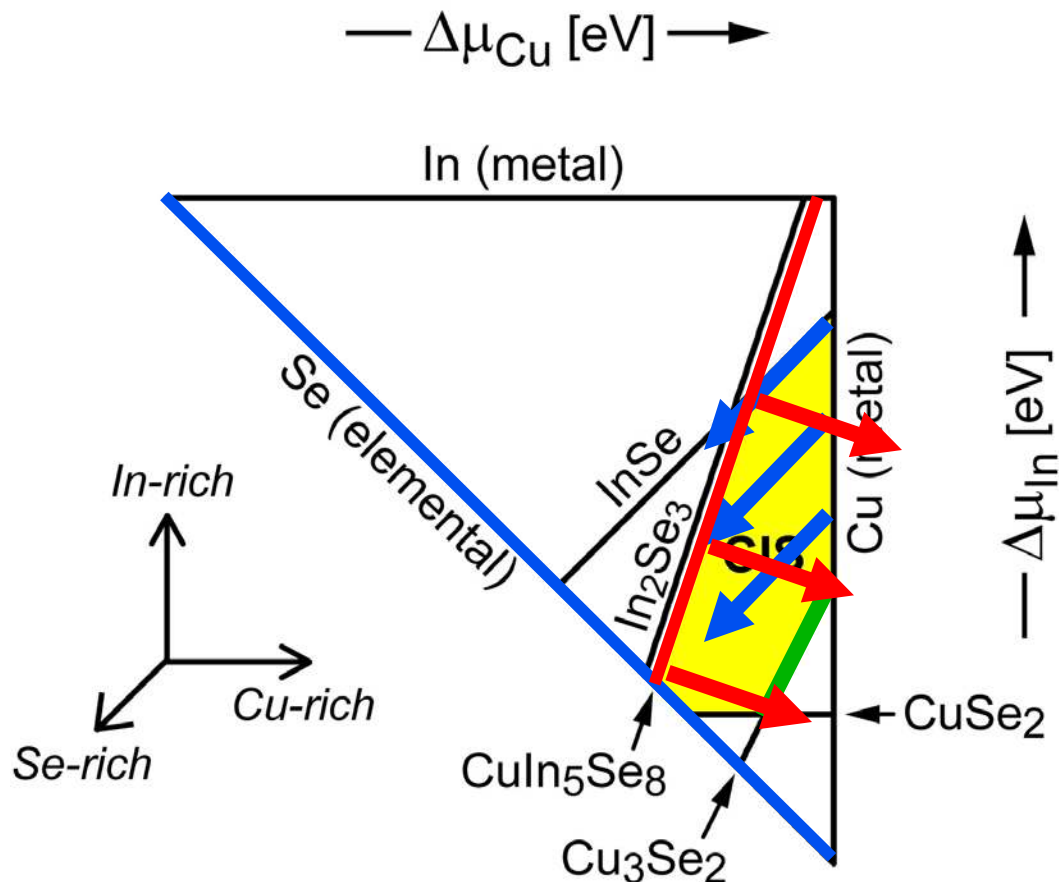
CuInSe₂ stability condition

$$\Delta\mu_{\text{Cu}} + \Delta\mu_{\text{In}} + 2\Delta\mu_{\text{Se}} = \Delta H_f(\text{CIS})$$

Competing phases

$$\text{e.g., } 3\Delta\mu_{\text{Cu}} + 2\Delta\mu_{\text{Se}} \leq \Delta H_f(\text{Cu}_3\text{Se}_2)$$

- Minimize In_{Cu} , Ga_{Cu} ,
($\text{In}_{\text{Cu}} - 2V_{\text{Cu}}$)
- Minimize V_{Se} , ($V_{\text{Se}} - V_{\text{Cu}}$)
- Cu-rich / Se-rich growth



Trade-offs for minimizing V_{OC} limiting defects

Minimizing defects:

Se-rich / Cu-rich

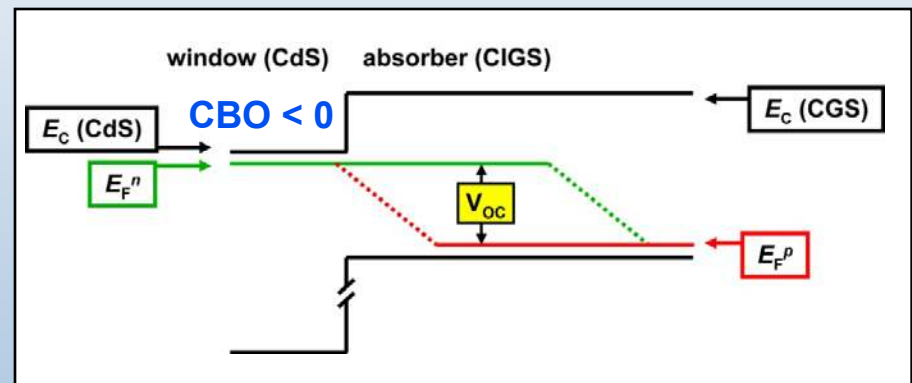
e.g., phase-equilibrium with Cu_3Se_2

Type inversion:

Se-poor / III-rich (Cu-deficient) [1]

Other causes of V_{OC} limit. :

band-offset [2], ...?



[1] S. Lany *et al.*, Appl. Phys. Lett. **86**, 042109 (2005)

[2] M. Morkel *et al.*, Appl. Phys. Lett. **79**, 4482 (2001)

Conclusions

- Intrinsic donor-type defects In_{Cu} , Ga_{Cu} , and V_{Se} , and their complexes with V_{Cu} cause metastability, but also act to limit V_{OC}
- Growth conditions which minimize these defects (Cu-rich/Se-rich) are very different from those currently used
- Overcoming V_{OC} limitation requires to address other issues and trade-offs

References

- S. Lany and A. Zunger, Phys. Rev. Lett. **100**, 016401 (2008)
S. Lany and A. Zunger, J. Appl. Phys. **100**, 113725 (2006)

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