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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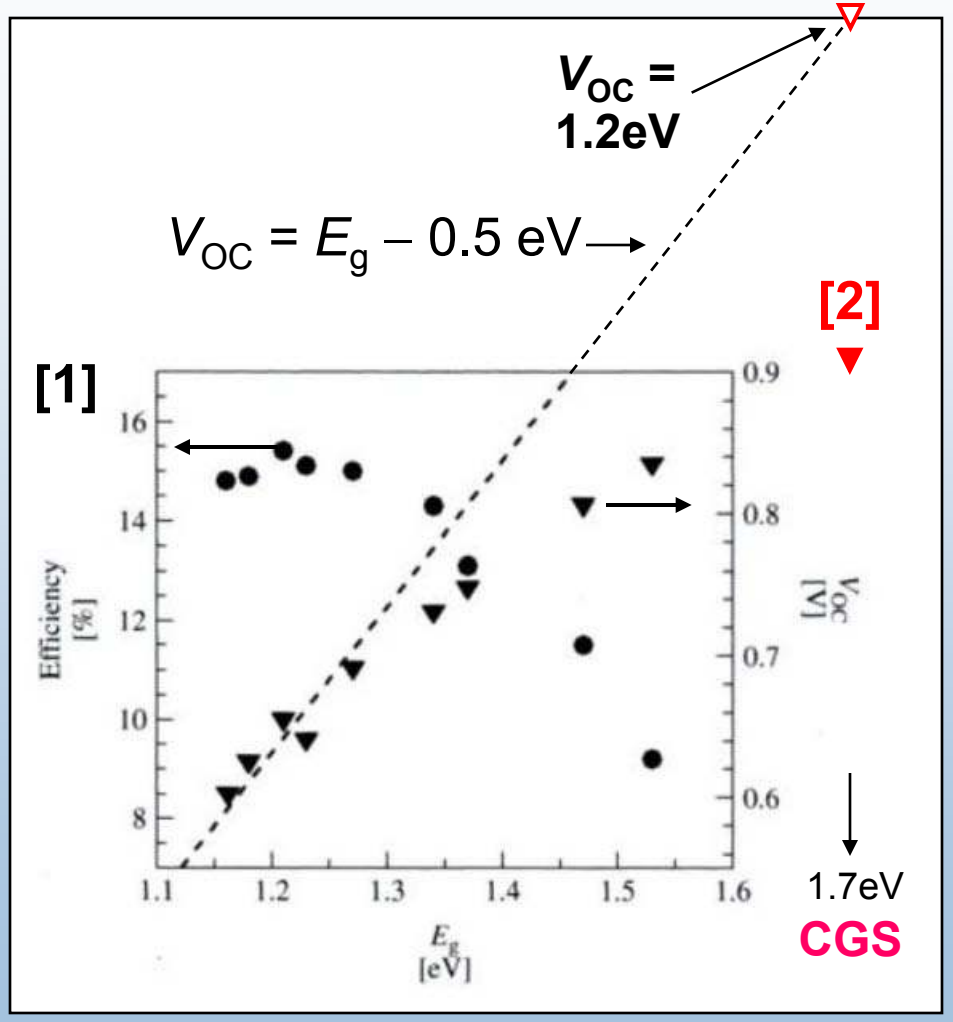
V_{OC} saturation in CIGS



Higher V_{OC}:

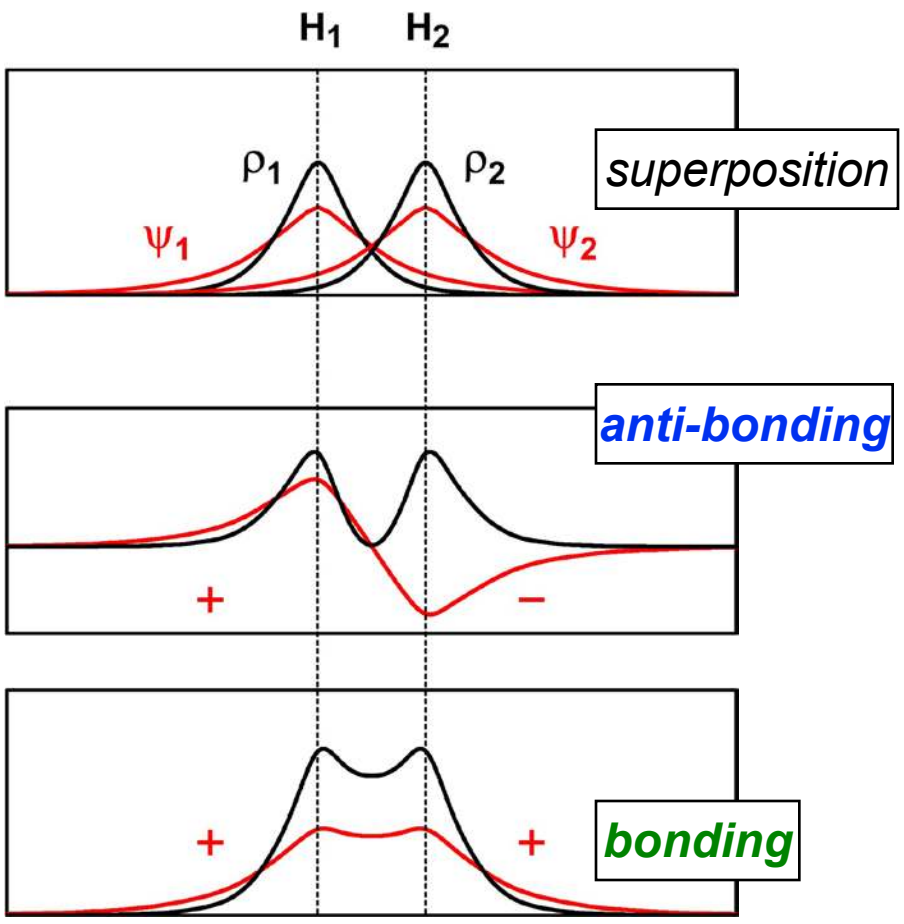
- Higher η for single-junction
- Needed for TF tandem
- Reason: Recombination due to deep defects [3]

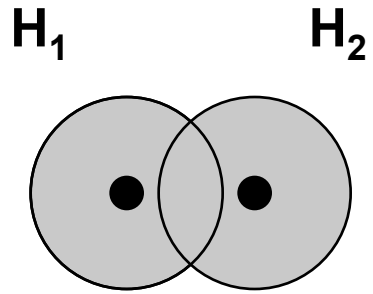
[1] W.N. Shafarman and L. Stolt, in: *Handbook of Photovoltaic Science and Engineering*

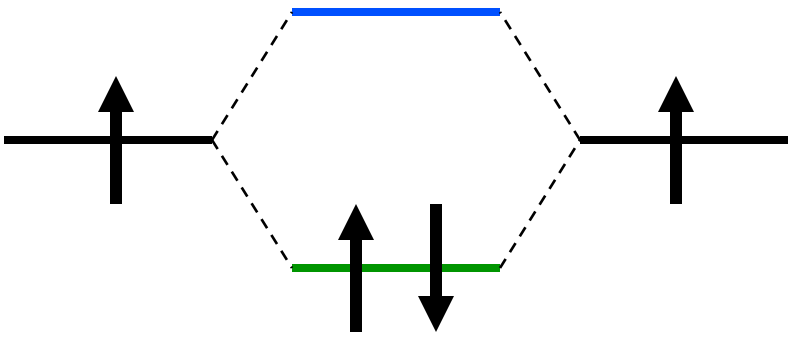
[2] R. Kniese, M. Lammer, U. Rau , M. Powalla, TSF **451-452**, 430 (2004).

[3] G. Hanna, A. Jasenek, U. Rau, H.W. Schock, TSF **387**, 71 (2001).

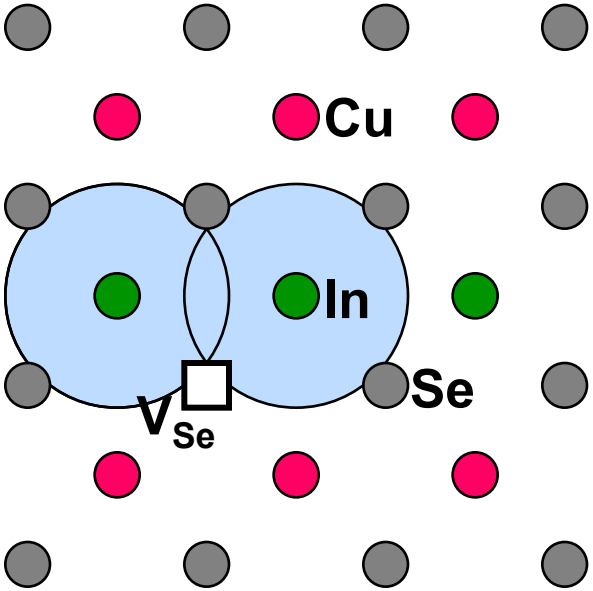
Defects levels (I) – Example: Orbital interaction in the H_2 molecule

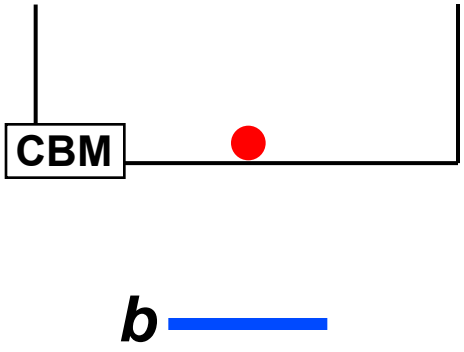


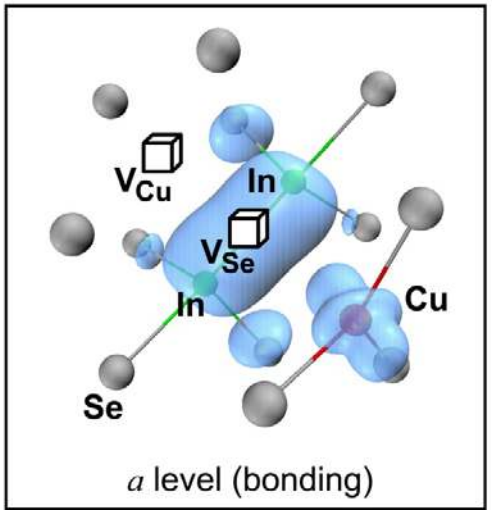




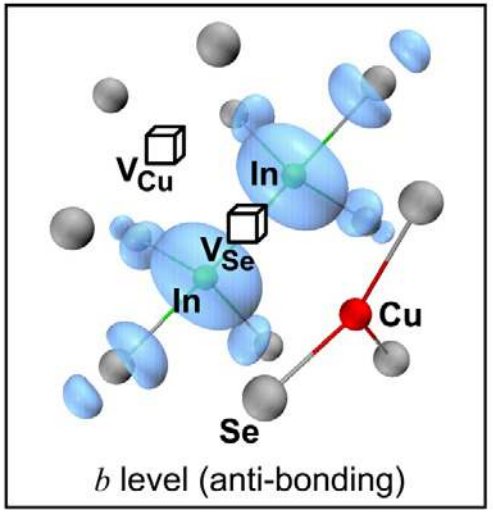
Defects levels (II): Se-vacancy in $CuInSe_2$



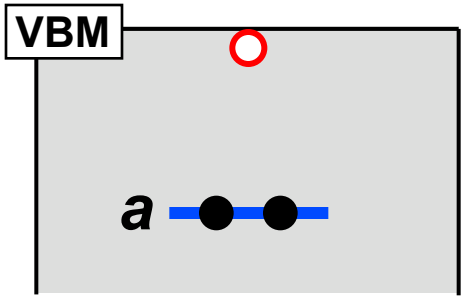




a level (bonding)

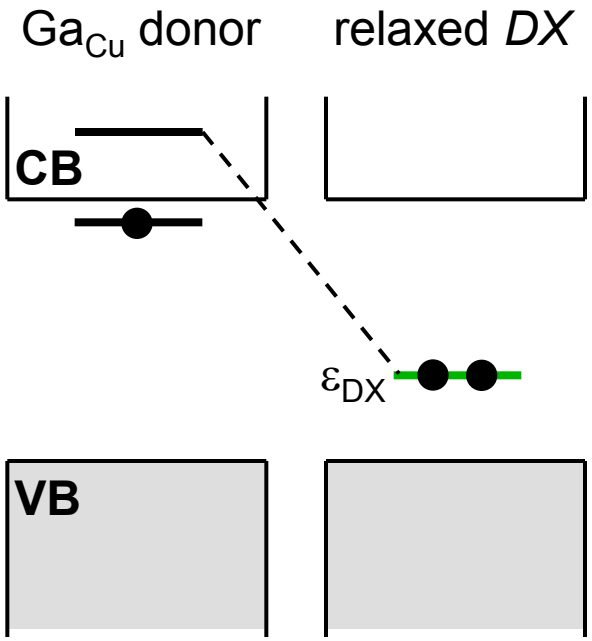


b level (anti-bonding)



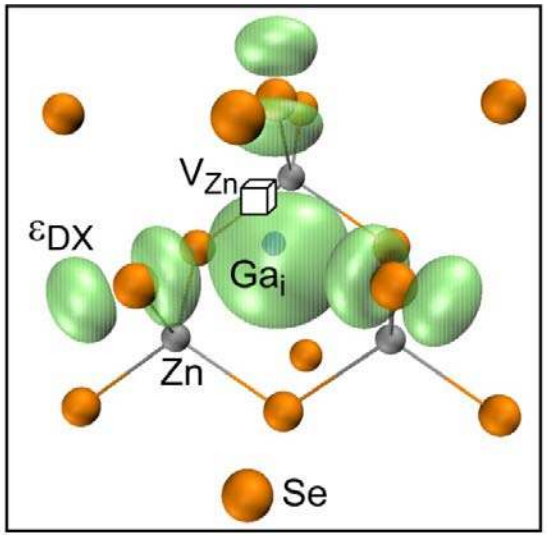
Intrinsic DX centers in CIGS

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



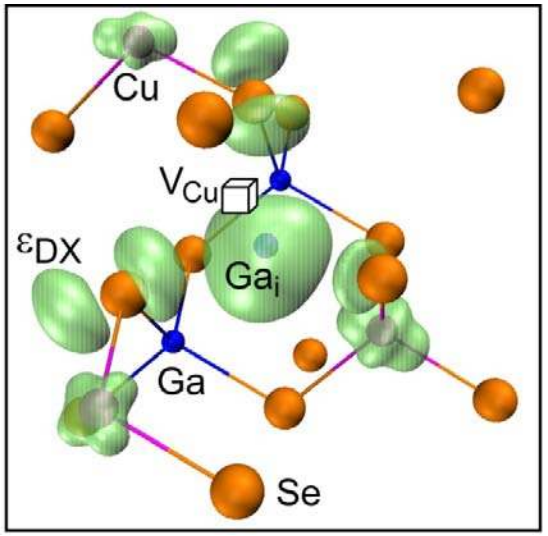
Extrinsic DX in II-VI

ZnSe:Ga_{Zn}



Intrinsic DX in CIGS

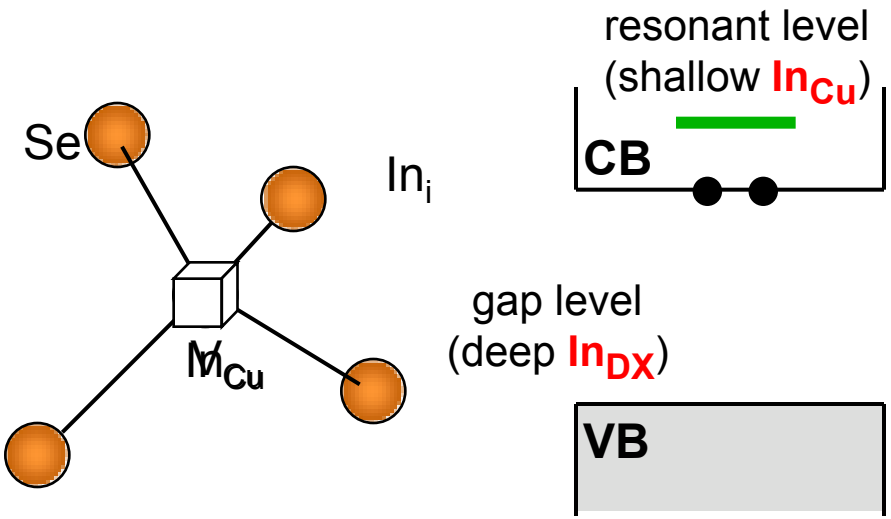
$CuGaSe_2$:Ga_{Cu}

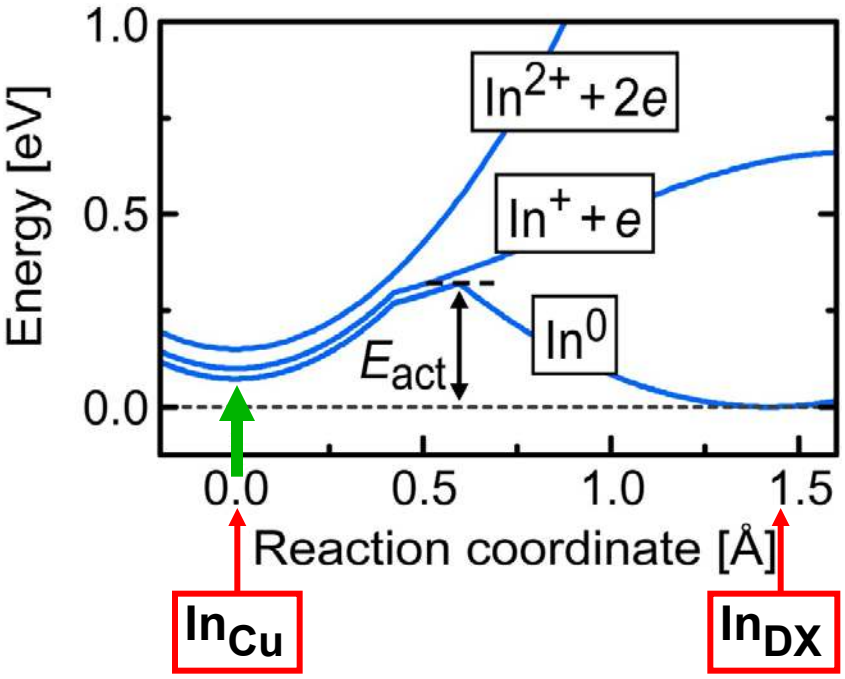


In II-VI, *DX* centers require **extrinsic** impurities
In CIGS, **native defects** (In_{Cu}, Ga_{Cu}) exhibit *DX* behavior

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

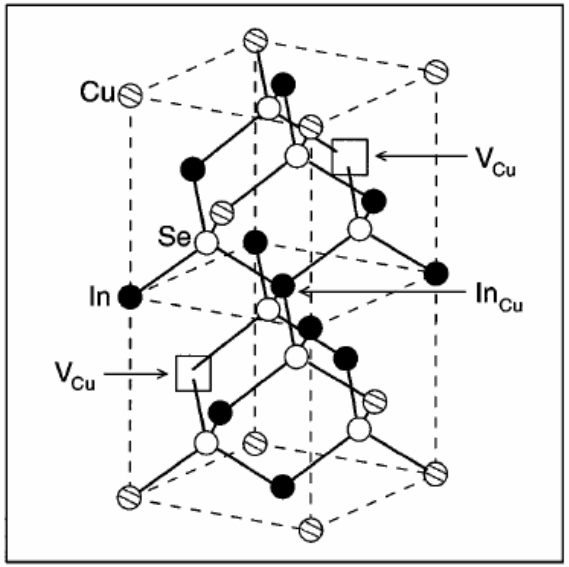
Evolvement of ionic structure, electron-level, and energy
during the transition into the deep DX state





Critical Fermi levels for electron-trapping

In_{Cu} (Ga_{Cu}) exists isolated or in complexes, e.g., (In_{Cu}-$2V_{Cu}$) [1]

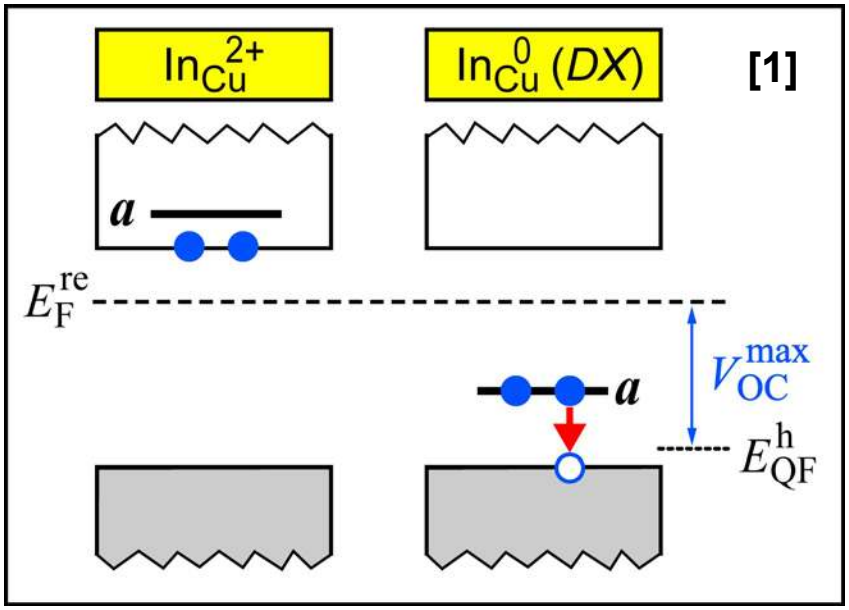


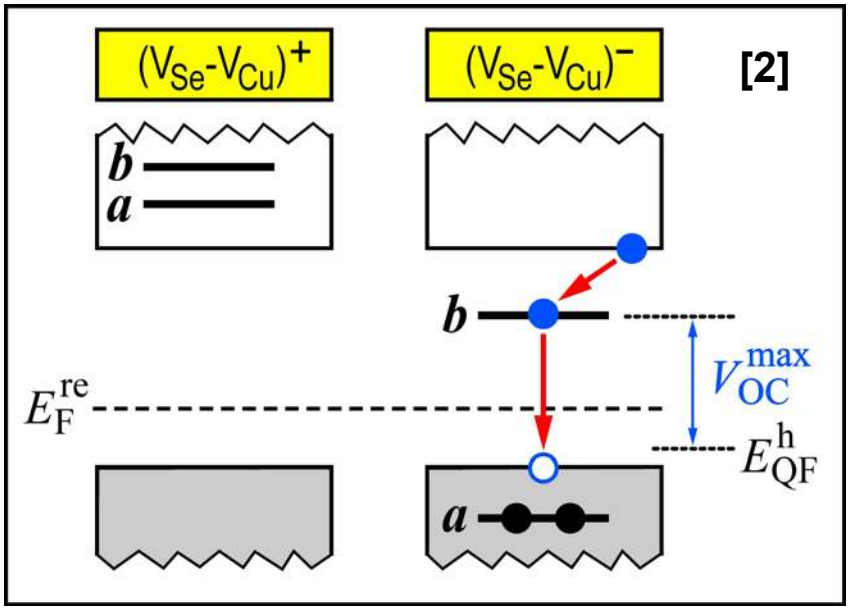
Transition	occurs above $E_F > E_V +$
$In_{Cu}^{2+} + 2e \rightarrow In_{DX}^{0}$	0.9 eV
$(In_{Cu}\text{-}V_{Cu})^{+} + 2e \rightarrow (In_{DX}\text{-}V_{Cu})^{-}$	1.1 eV
$(In_{Cu}\text{-}2V_{Cu})^{0} + 2e \rightarrow (In_{DX}\text{-}V_{Cu})^{2-}$	1.3 eV

Electron-trapping due to DX centers occurs mainly in wider-gap $CuIn_{1-x}Ga_xSe_2$ alloys with $x \geq 0.3$

[1] S.B. Zhang, S.-H. Wei, and A. Zunger, Phys. Rev. Lett. **78**, 4059 (1997).

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

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

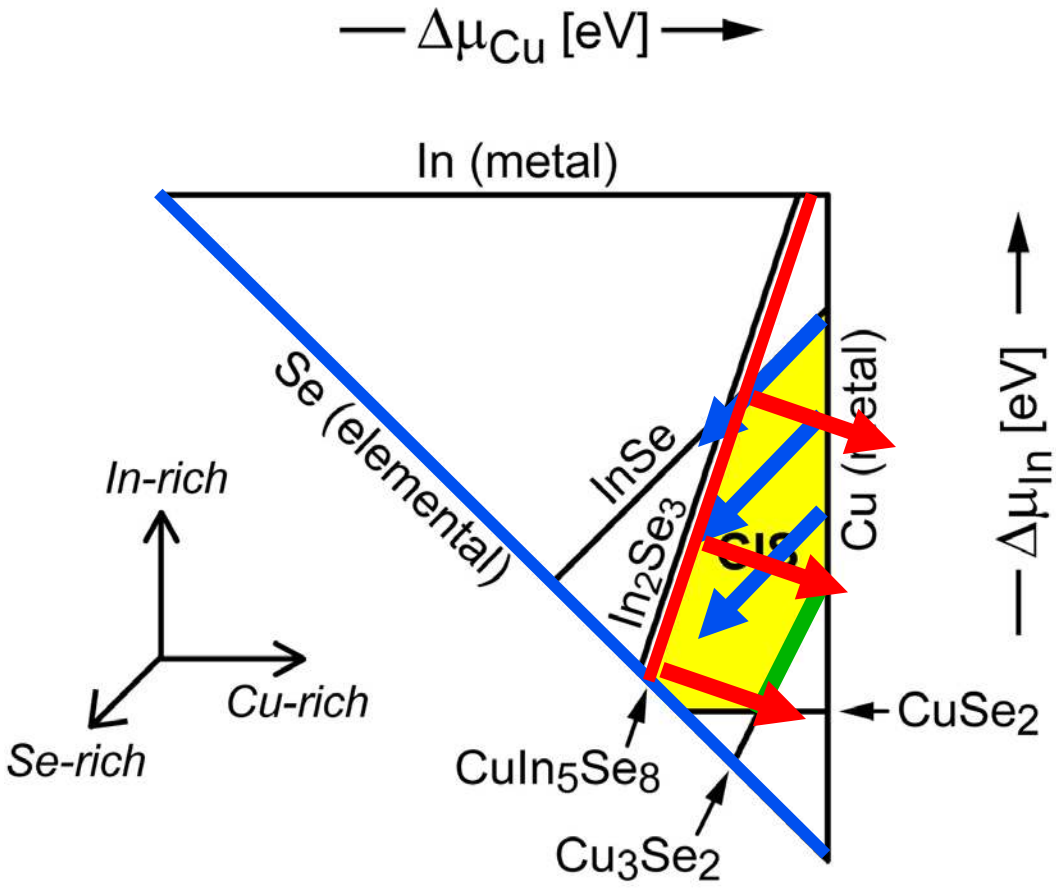
$CuInSe_2$ stability condition

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

Competing phases

e.g., $3\Delta\mu_{Cu} + 2\Delta\mu_{Se} \leq \Delta H_f(Cu_3Se_2)$

- **Minimize In_{Cu}, Ga_{Cu}, (In_{Cu}-$2V_{Cu}$)**
- **Minimize V_{Se}, (V_{Se}-V_{Cu})**
- **Cu-rich / Se-rich growth**

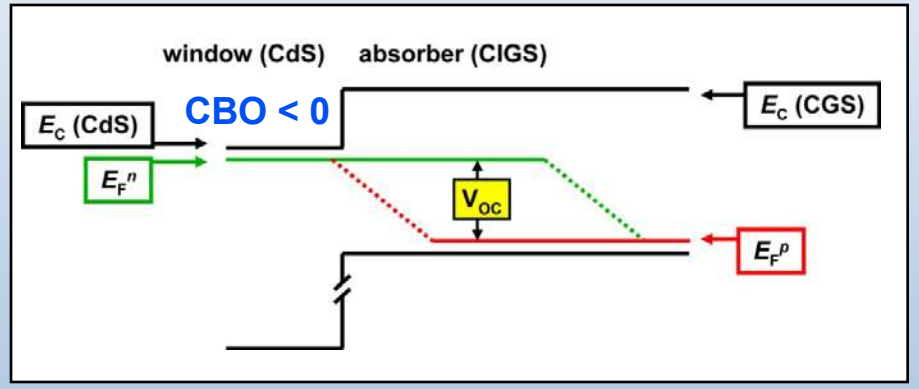


Trade-offs for minimizing V_{OC} limiting defects

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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