First principles modelling of extended defects

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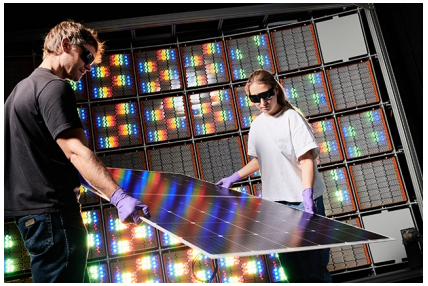
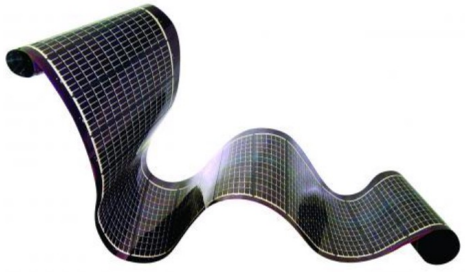
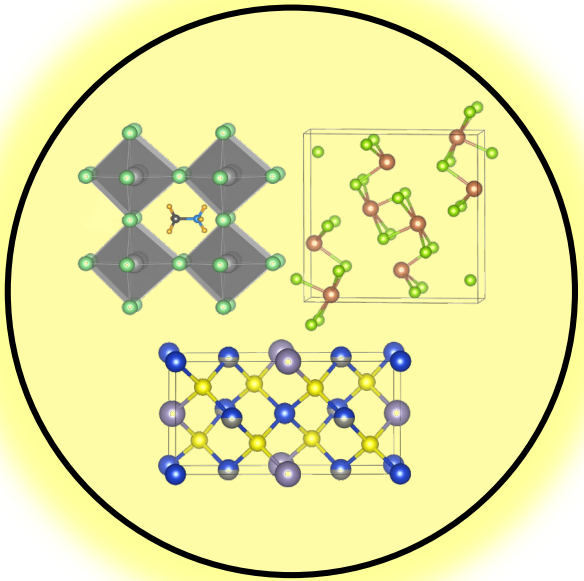
Introduction

- Thin-film solar absorbers for PV: tandem, indoor, flexible…
- Require efficiency, stability, tunability, earth-abundance, low cost…
- First principles predictive modelling can help guide materials optimisation and discovery
- Prediction of ideal single crystal properties now routine (often to very high accuracy)

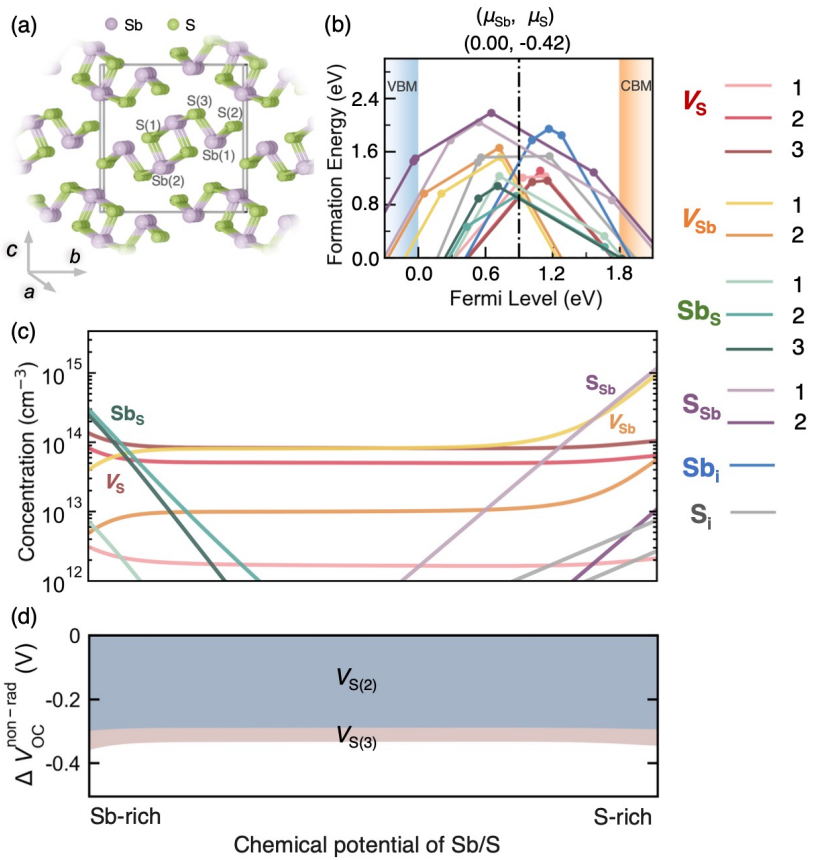






Point defects

- Point defects are unavoidable and affect properties (e.g., optical and electrical)
- To understand real materials we must model them
- Methods for first principles modelling of point defects well established (periodic and embedding approaches)
- Not yet completely routine but point defects in bulk crystals modelled widely

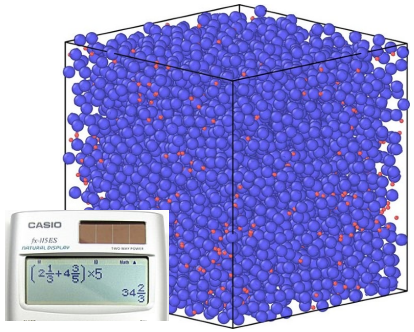


Xinwei Wang, Seán R. Kavanagh, Aron Walsh, https://doi.org/10.48550/arXiv.2410.10560 (2024)

Real materials

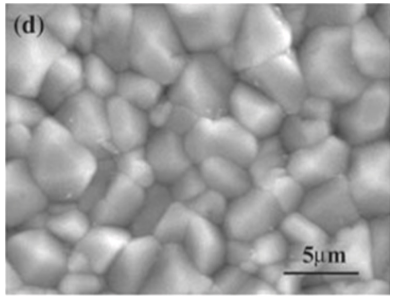
- Real materials are more complex: amorphous, nanostructured, polycrystalline
- Most thin-film absorbers are polycrystalline and so grain boundary defects are ubiquitous
- Important to consider impact on prospective material performance

***a*-Si**



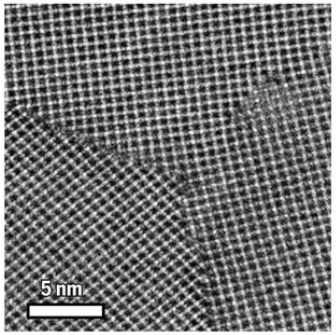
A. Diggs et al, Communications Materials **4**, 24 (2023)

***poly*-CdTe**



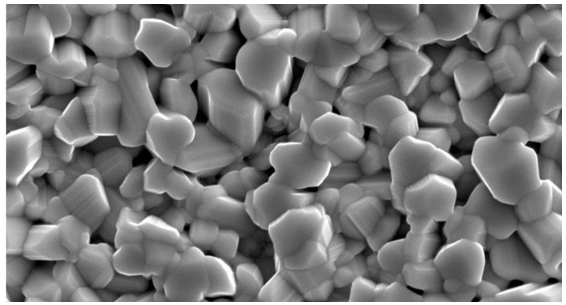
X. Z. Wu, Sol. Energy **77** 803–14 (2004)

***poly*-$FAPbI_3$**



M.U. Rothmann et al, Science **370** eabb5940 (2020)

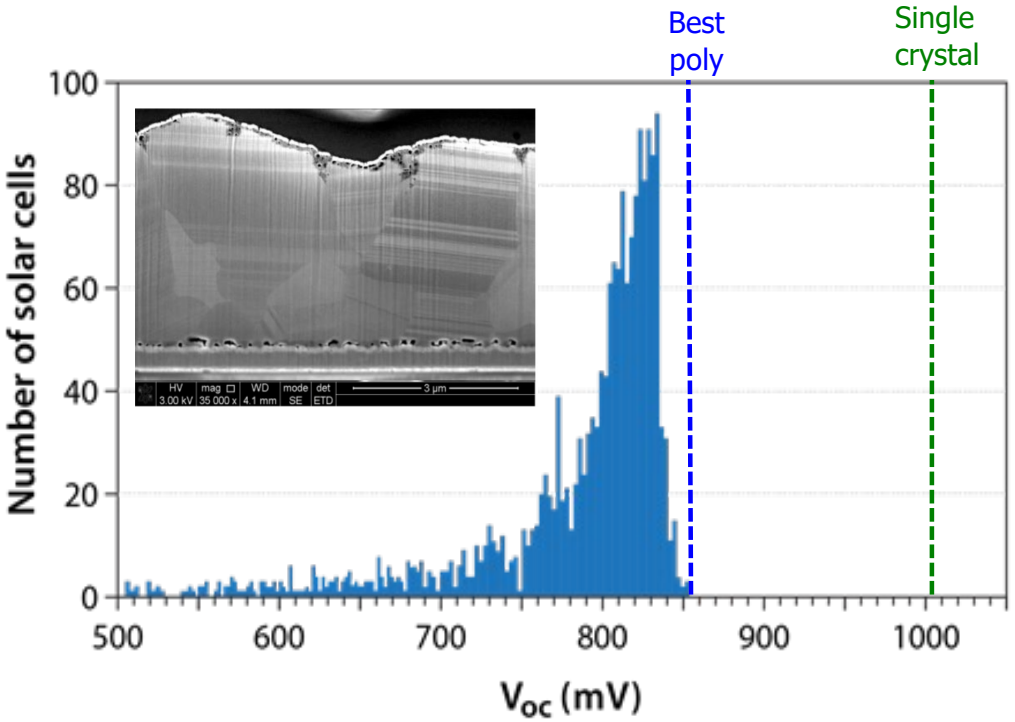
***poly*-Sb_2Se_3**



O.S. Hutter et al., Solar Energy Materials and Solar Cells **188**, 177 (2018)

Impact of grain boundaries in CdTe

- Grain boundaries cause significant V_{OC} deficit (due to enhanced non-radiative recombination)
- [Cd/Mg]Cl_2 treatments reduce negative impact but do not eliminate
- Essential to include extended defects like grain boundaries in screening approaches
- Preferable to identify materials where GBs are intrinsically less deleterious

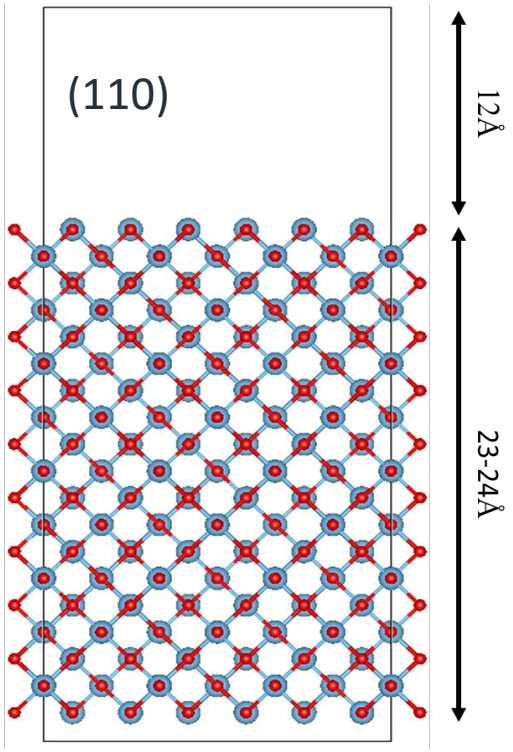


Significant V_{OC} deficit for poly-CdTe relative to single crystal

J.M. Burst et al, Nature Energy **1**, 16015 (2016)

First principles approaches for modelling extended defects

- ***Density functional theory*** is a good compromise between accuracy and computational cost
- Predict structure of materials in 3D (dependence on conditions)
- Predict corresponding properties (including those that are difficult to measure directly)
- Well established methods for modelling surfaces using the slab approach



Supercell for modelling the (110) anatase TiO_2 surface

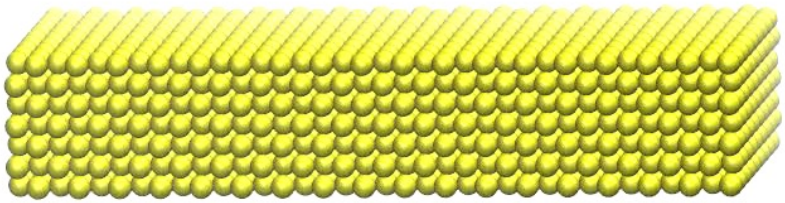
J.J. Carey and K.P. McKenna, J. Phys. Chem. C **122**, 27540 (2018)

Modelling grain boundaries

- Direct MD simulation of crystallization or film growth (only viable for interatomic potentials)

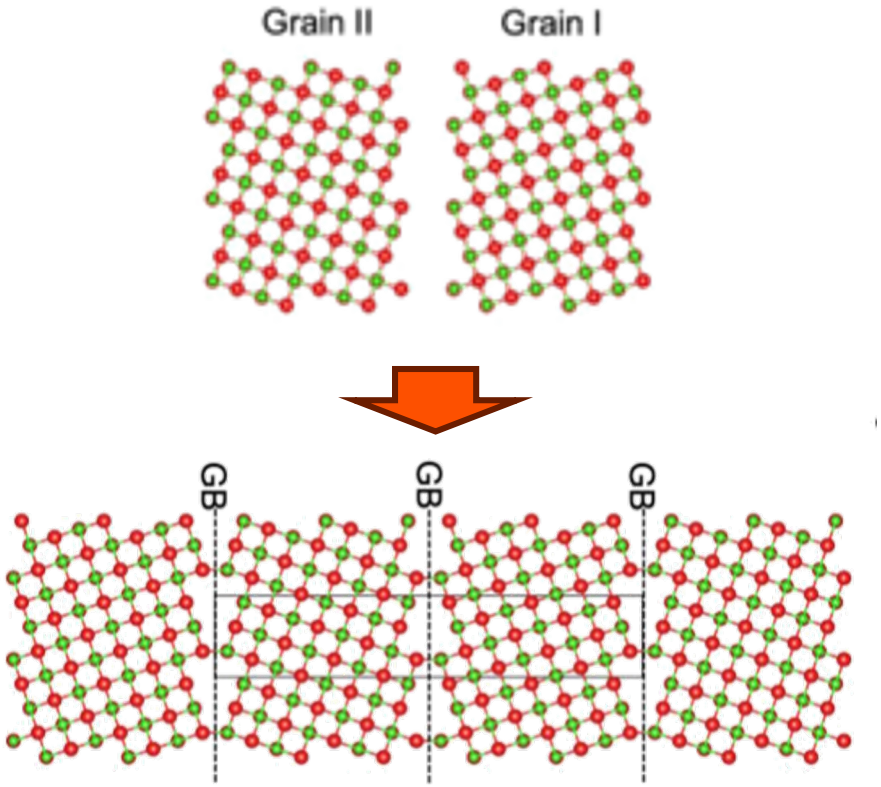
Fe

Cu



Modelling grain boundaries

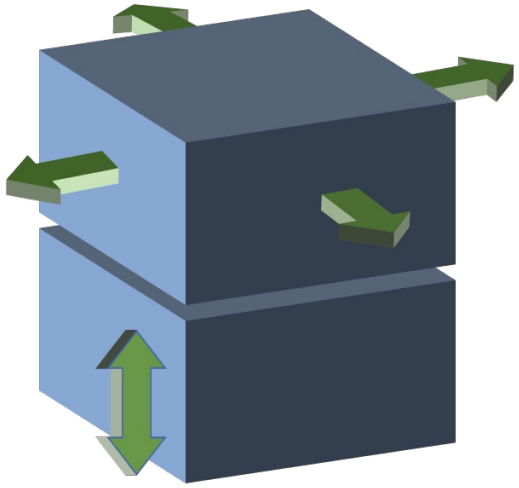
- Direct MD simulation of crystallization or film growth (only viable for interatomic potentials)
- Using DFT can model specific planar interfaces between two oriented grains
- Various codes/tools available for construction of models: Metadise, Pymatgen, GBMaker



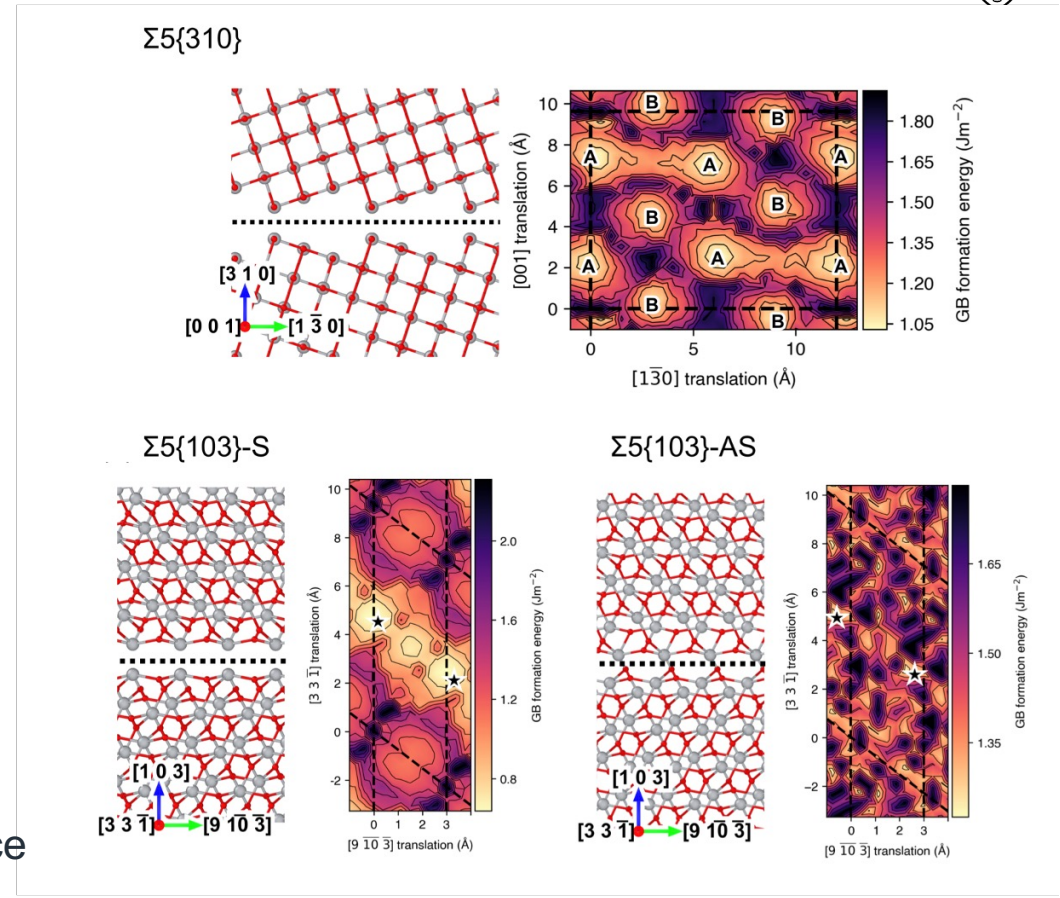
G. W. Watson *et al*, Faraday Trans. **92**, 433 (1996)

A. Kerrigan and K. P. McKenna, GBMaker v1.0.0 (Github, 2022) (2022). https://doi.org/10.5281/zenodo.6334740

Gamma surface approach

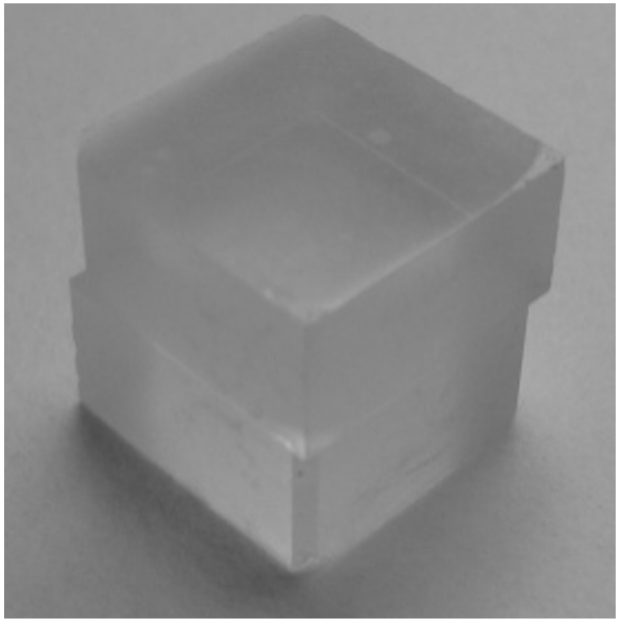


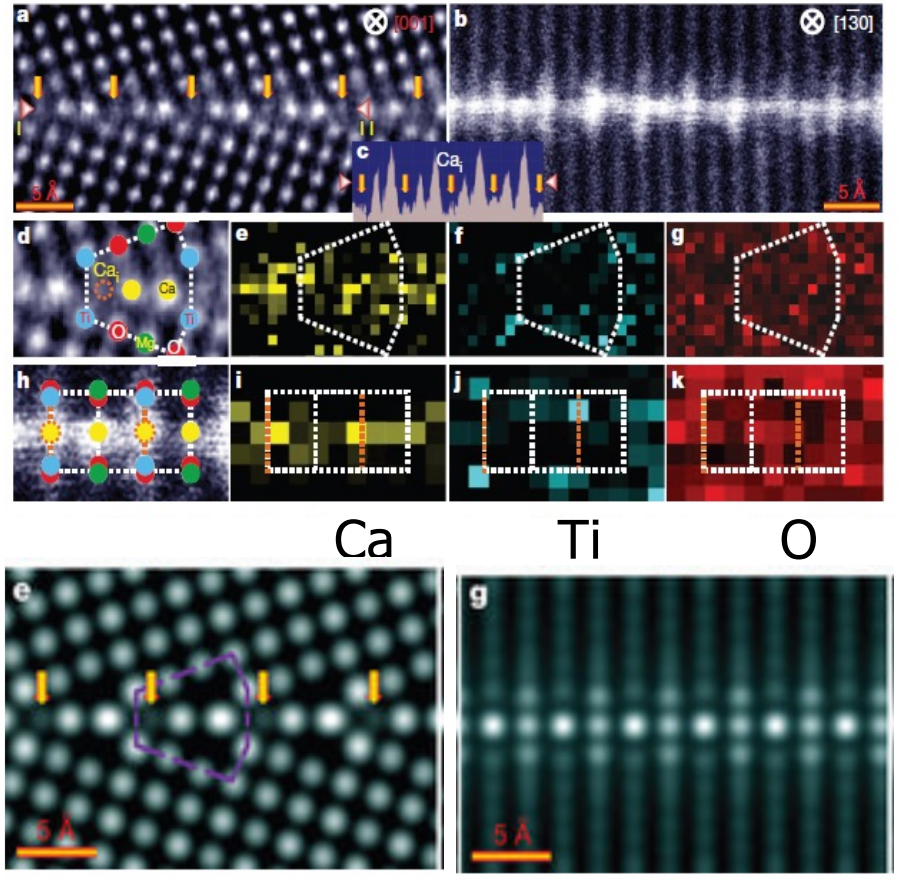
Minimise energy with respect to intergrain translation/dilation, addition/removal of ions at interface



J. A. Quirk, B. Miao, B. Feng, G. Kim, H. Ohta, Y. Ikuhara and K. P. McKenna, Nano Letters **21**, 9217 (2021)

Analogous to the bicrystal approach

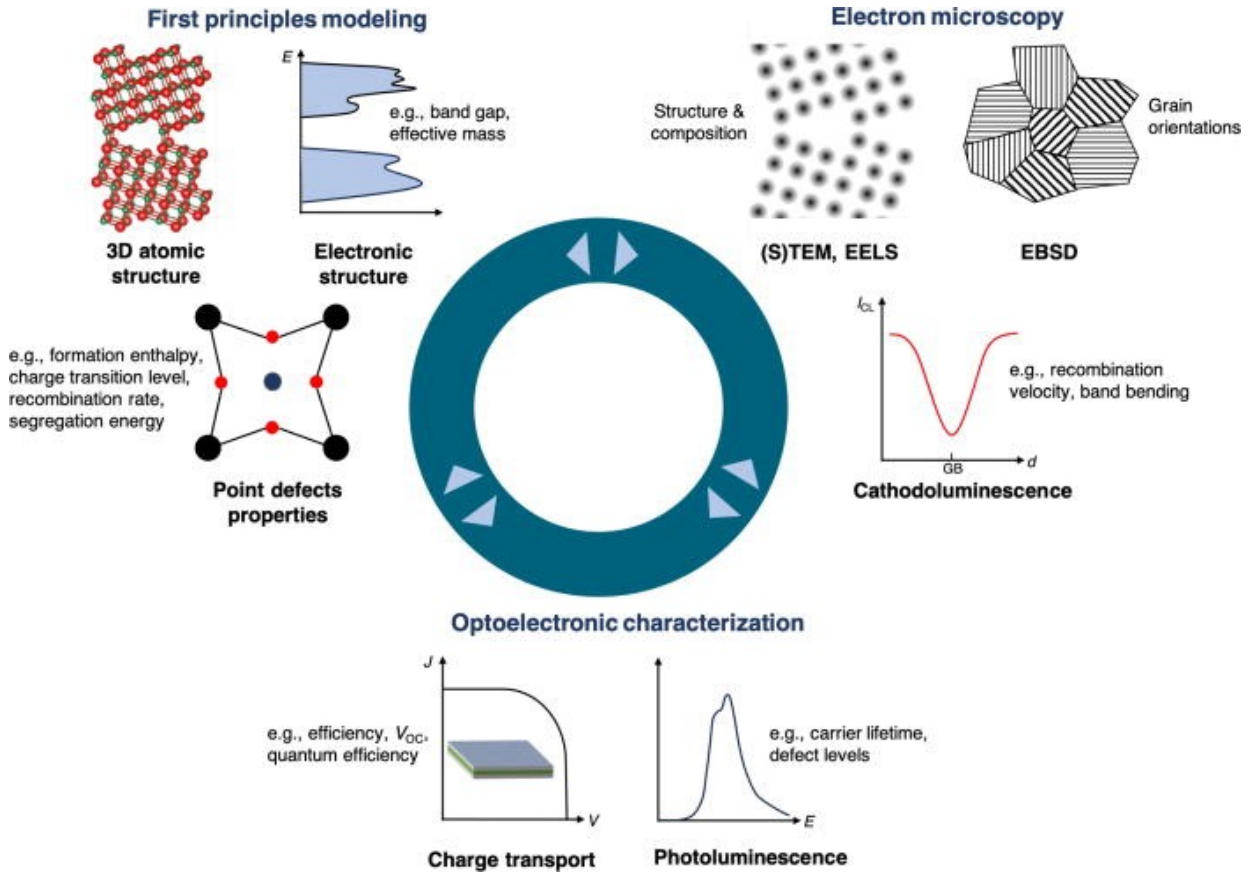




K.P. McKenna *et al*, Nat. Mater. **7**, 859 (2008)
K.P. McKenna *et al*, Nat. Commun. **5**, 5740 (2014)

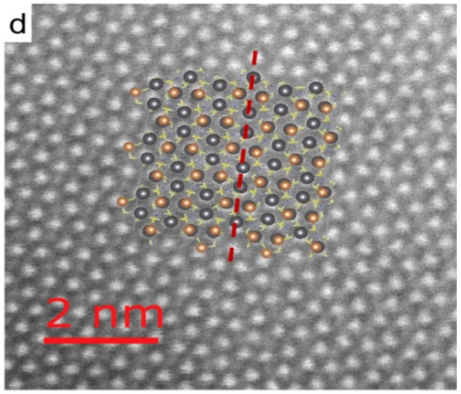
Z. Wang, M. Saito, K. P. McKenna et al, Nature **479**, 380 (2011)

Complementary techniques



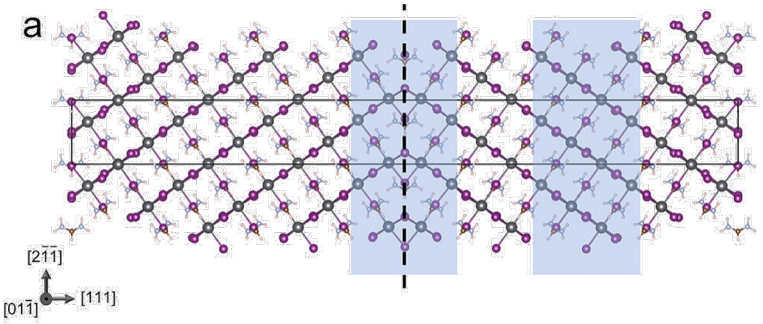
Grain boundaries in polycrystalline materials for energy applications: first principles modeling and electron microscopy
J. Quirk, M. Rothmann, W. Li, D. Abou-Ras, K. P. McKenna, Appl. Phys. Rev. **11**, 011308 (2024)

$CuPbSbS_3$ & $Cu3AsS_4$



O. M. Rigby et al, J. Appl. Phys. 132, 185001 (2022)

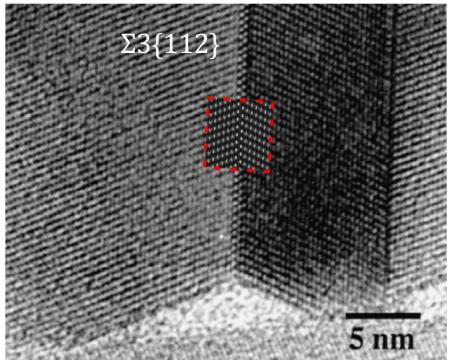
Lead halide perovskites



K. P. McKenna, ACS Energy Lett. **3**, 2663 (2018)

M. U. Rothmann et al, Adv. Mater. Inter. (2023)

TiO_2

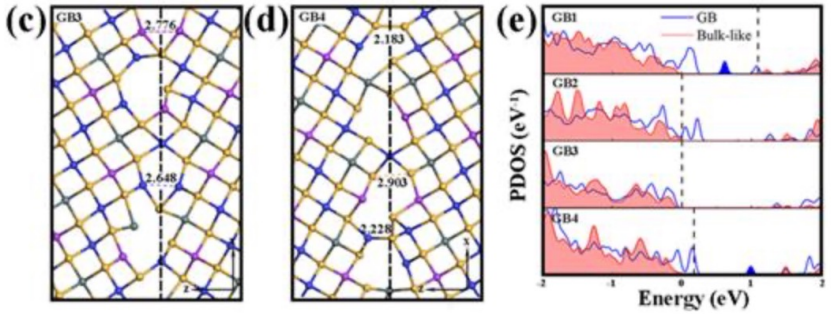


J. A. Quirk et al, Nano Lett. 21, 9217 (2021)

G. Schusteritsch et al, Nano Lett. 21, 2745 (2021)

J. Quirk et al, Adv. Theory Simul. 2, 1900157 (2019)

$Cu_2ZnSn(S_xSe_{1-x})_4$

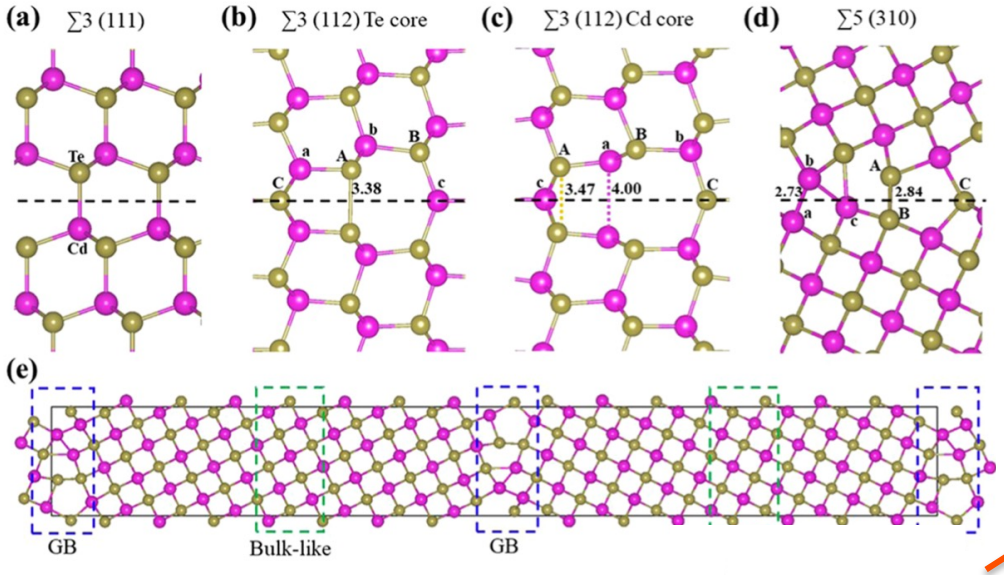


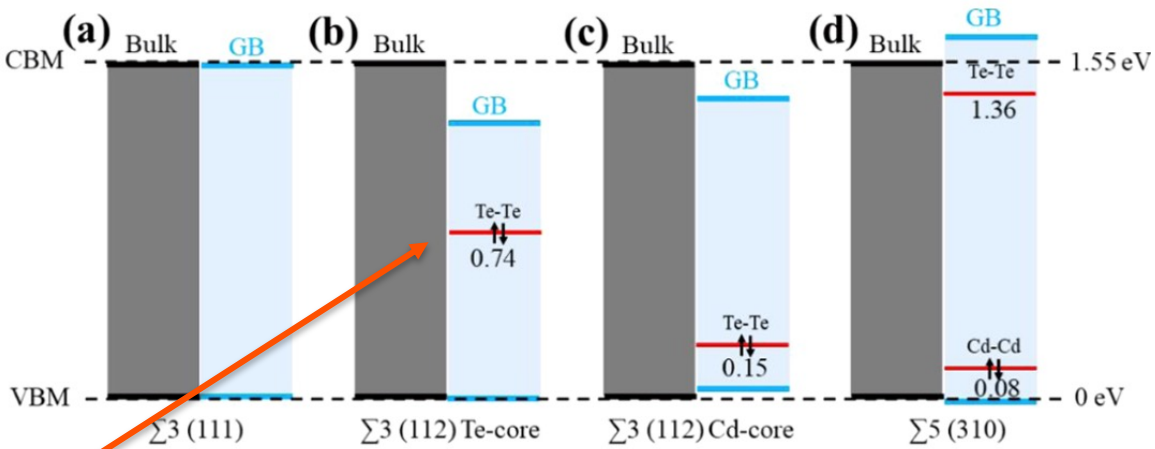
N-J. Hao et al, J. Appl. Phys. 133, 145002 (2023)

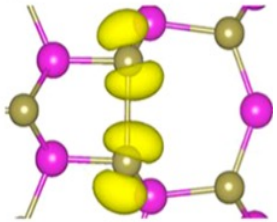
C. Tong et al, J. Phys. Chem. Lett. 11, 10463 (2020)

B. Mendis et al, J. Mater. Chem. A 6, 189 (2018)

Example: CdTe grain boundaries







Dangling bonds at grain boundary and deep levels in gap (recombination centres)

C. Tong and K. P. McKenna, Journal of Physical Chemistry C **123**, 23882 (2019)

Experimental information – EBSD and IBIC

- **Σ**3 twin boundaries common as well as more general GBs
- Untreated cells: GB contrast is dark suggesting high recombination but twin boundaries benign (also confirmed by CL)
- Treated cells: GB contrast bright (more than bulk even, suggesting reduced reduced recombination and possibly beneficial band bending)

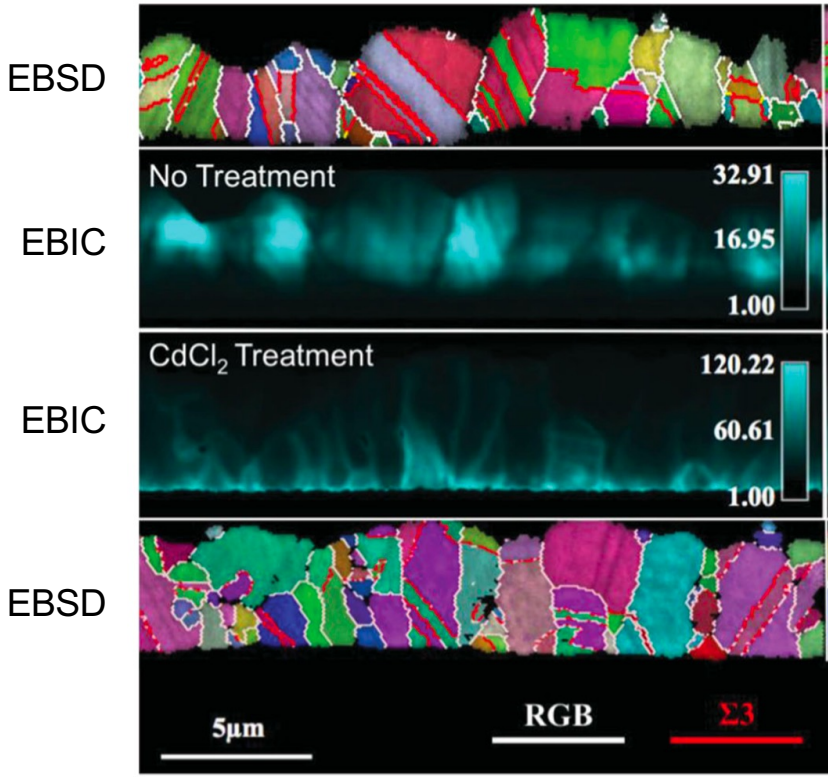
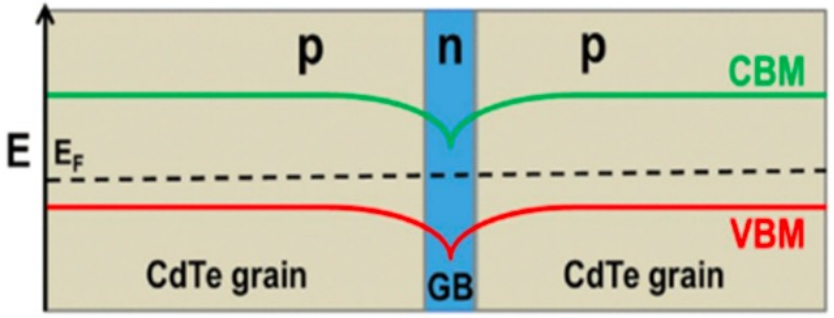


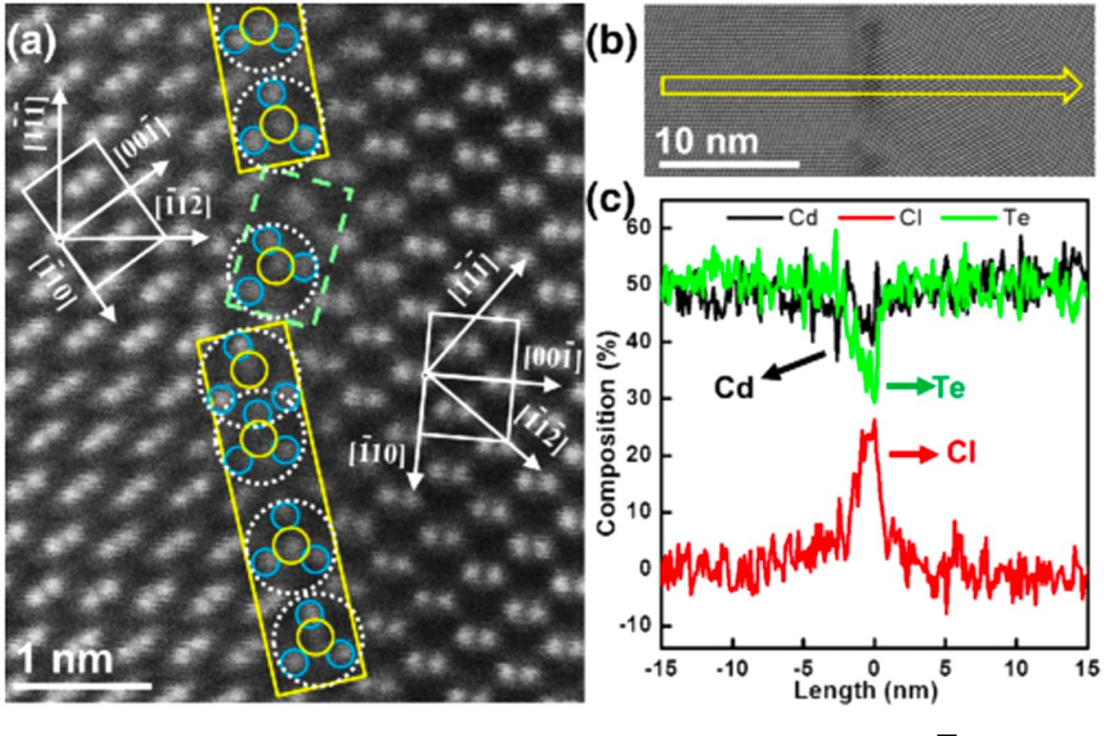
Figure 7. EBIC and EBSD maps of untreated, $CdCl_2$ treated, Cu treat
from [75].

J. D. Poplawsky *et al*, Adv. Energy Mater. **4** 1400454 (2014)

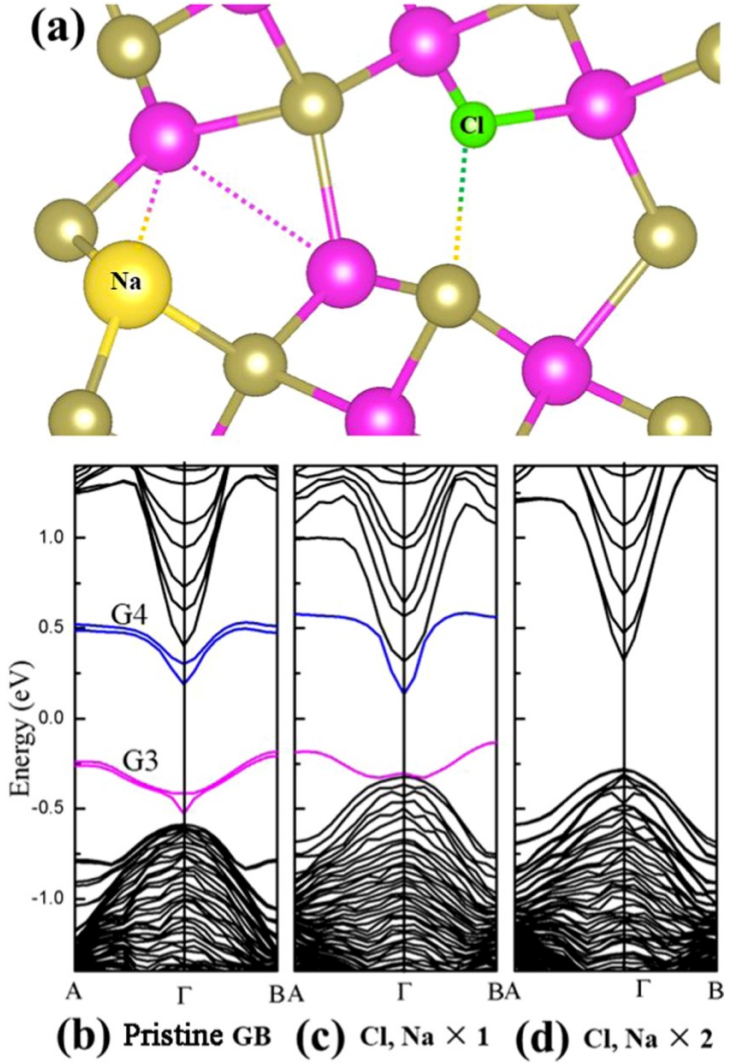
Experimental information – STEM

- Cl enrichment and Te depletion at GBs suggesting Cl_{Te} substitution
- Suggest local n-doping and downward band bending at GB (improved carrier separation and collection)





C. Li *et al*, Phys. Rev. Lett. **112**, 156103 (2014)

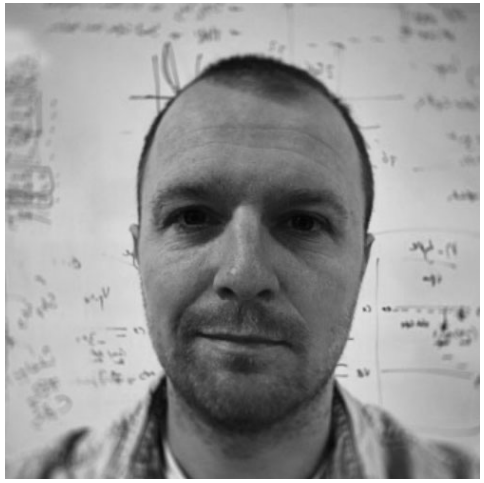


Co-doping with Na and Cl predicted to remove Cd-Cd and Te-Te dangling bond states

C. Tong and K. P. McKenna, Journal of Physical Chemistry C **123**, 23882 (2019)

GB challenges

- The excellent review on CdTe GBs by Jon Major[1] highlights the complexity of polycrystalline films:
  - Impurities unavoidable in processing (e.g., Cu, O, S, As, Na, P, F)
  - For many characterization methods with the necessary spatial resolution, sample preparation and geometry can affect results/interpretation (e.g., EBIC, CL, SPM, PL)
  - As a result, while consensus Cl treatments improve performance, conflicting models explaining why (down/up band bending, improved current collection +/- reduced recombination)
  - Role of GBs in limiting doping unknown

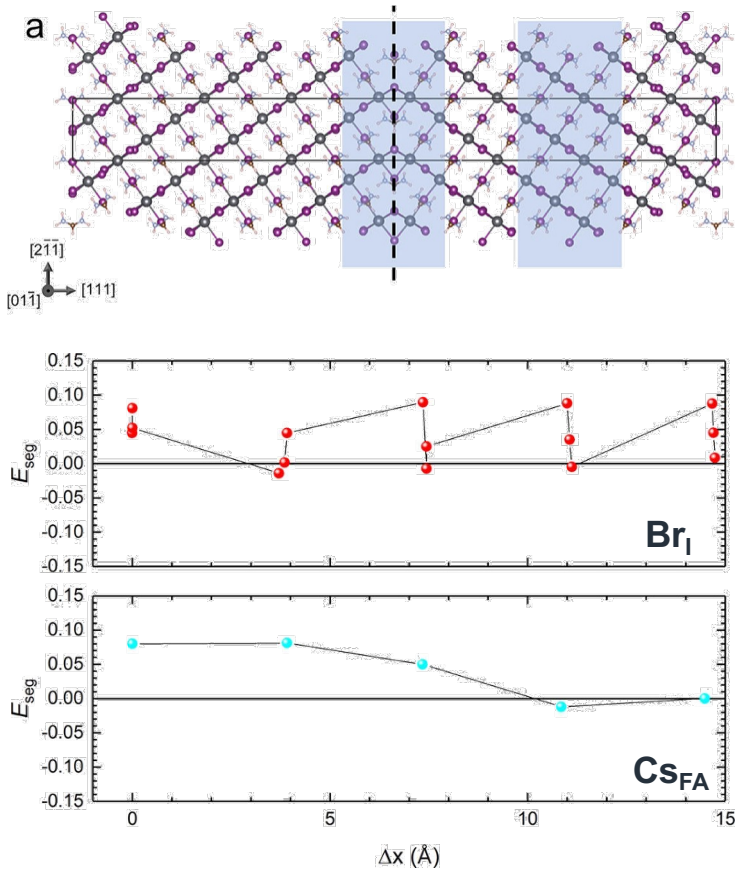


"An overarching conclusion to be drawn from this review is that there remains a level of complexity to the characterization of GBs in solar cells that is yet to be fully overcome."

[1] J. Major, Semicond. Sci. Technol. **31** 093001 (2016)

Modelling challenges: point defect equilibrium

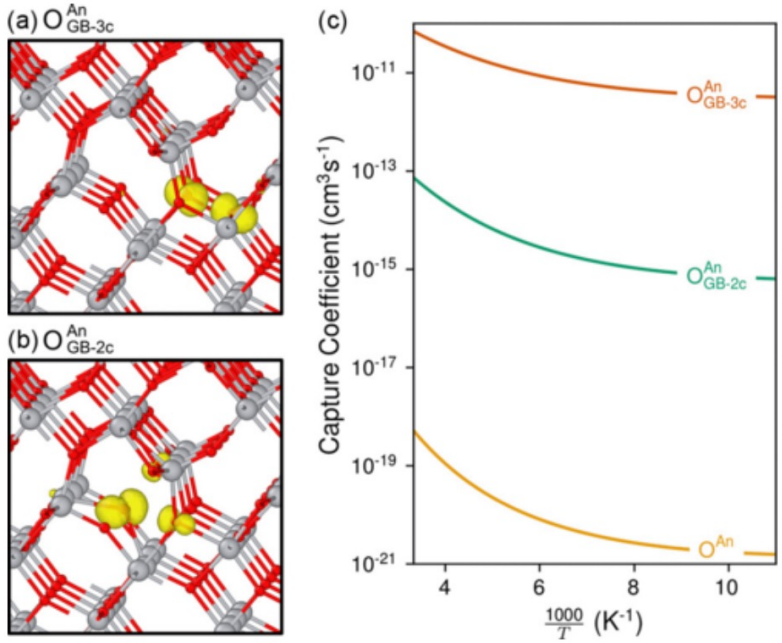
- Current approach:
  - Construct pristine GB
  - Add point defects into bulk and GB regions to assess stability and electronic properties
- Issues:
  - Only appropriate in very dilute limit (at GBs concentrations can be high)
  - Exhaustive structure searching usually not feasible (may miss stable configs)
  - Need self-consistent equilibrium between bulk and GB including electrostatics (band bending)
  - Should allow structure of GB region to equilibrate according to composition (i.e., a grand canonical interface free-energy minimization)



K.P. McKenna, ACS Energy Lett. **3**, 2663 (2018)

Modelling challenges: GB properties

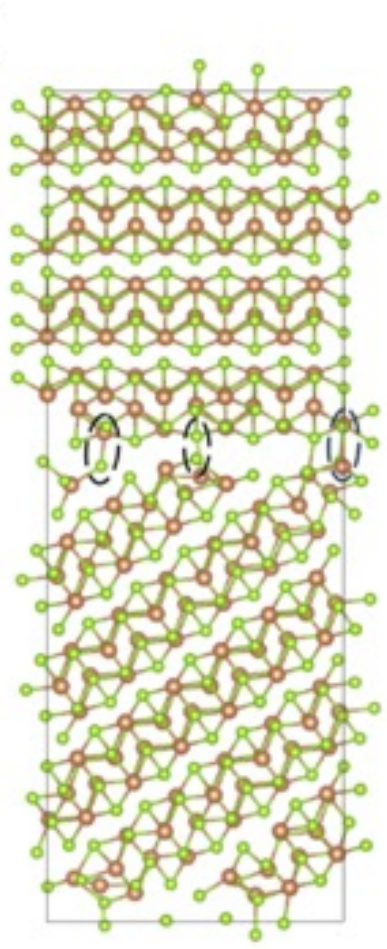
- Current approach:
  - Usually limited to hybrid functional calculation of electronic properties
  - One example where non-radiative recombination has been assessed[1]
- Issues:
  - Supercells with large numbers of atoms makes higher levels of theory challenging



[1] J. A. Quirk and K P. McKenna, Phys. Rev. Research **5**, 023072 (2023)

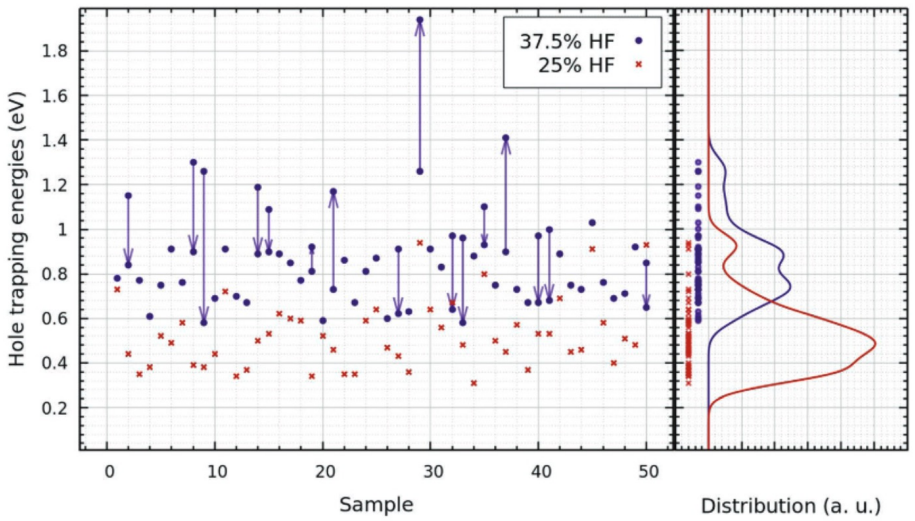
Modelling challenges: periodicity

- Current approach:
  - Employ periodic supercells to model symmetric or asymmetric GBs
- Issues:
  - Types of GBs that can be considered limited by size of supercell
  - Level of theory to be employed restricts even further (e.g., hybrid)
  - Lower symmetry extended defects (like GB steps or triple junctions) which are very common almost impossible to model
  - Need accurate and flexible non-periodic approaches, e.g. embedding with ML potentials and QM/MM interface regions



Modelling challenges: statistics

- Current approach:
  - Model a handful of stable boundaries (either those observed or with high symmetry and low formation energy)
- Issues:
  - A small number of damaging defects may dominate performance
  - Would like to predict a distribution of properties reflecting the distribution of extended defects in real materials

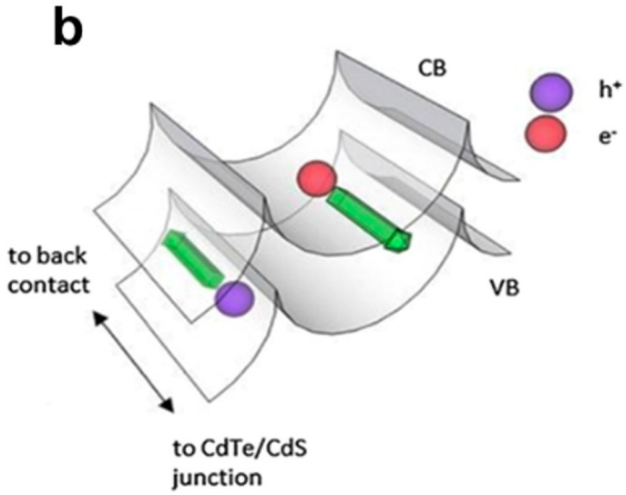


Distribution of hole trapping energies in *a*-ZnO

D. Mora-Fonz *et al*, Adv. Electron. Mater. 6, 1900760 (2020)

Linking to device simulation

- If we could do all (or some) of the above we would have:
  - A distribution of grain orientations with defined carrier transport properties and point defect limited recombination rates
  - A distribution of rates of recombination corresponding to different GBs/triple junctions
  - A distribution of electrostatic potential profiles corresponding to different GBs = affects carrier transport (inhomogeneous)
- These predictions would help in addressing the experimental characterization challenge
- How would we link this information to device simulation?



Conclusions

- Even for CdTe (a material with more information on GBs from experiment and theory than almost any other) we are not currently able to link predictive models of GB to PV device simulations
- However, we do know single crystal properties + point defects are not representative of poly-CdTe films (cannot predict V_{OC} or doping limits)
- Many modelling challenges still to overcome
- Essential if we want to use modelling to guide materials development

Acknowledgements

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COST and RenewPV

Computational time:

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