Rational Design of Wide Band Gap Buffer Layers for High-Efficiency Thin-Film PV

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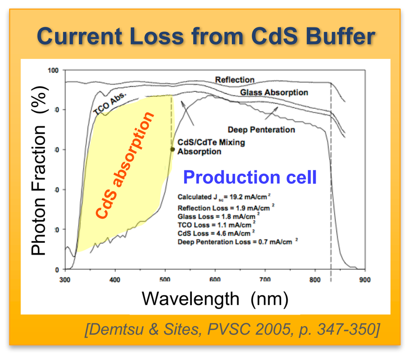
SunShot BRIDGE (Bridging Research Interactions through Collaborative Development Grants in Energy)

1. Introduction

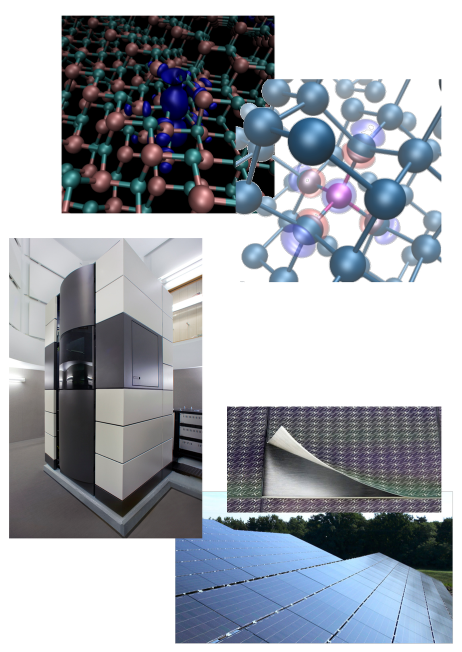
- Efficiency of production thin-film PV is significantly impacted by absorption in buffer layer (CdS)
- Higher performance **wide band gap buffer material** is needed



- **Objectives:**
  - Combine theory and characterization to enable optimization of new buffer materials
  - **Focus on defects & interfaces**

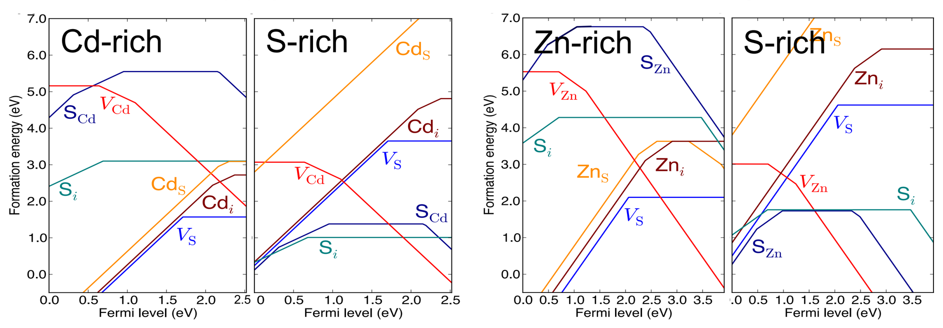
Methods

- **First-principles materials simulations** of defect properties using hybrid functional DFT
- **Atomic-scale imaging & compositional analysis** using aberration-corrected scanning transmission electron microscopy
- **World-class manufactured materials** from MiaSolé Hi-Tech using all-PVD roll-to-roll process



2. Theoretical Basis of Effects of Point Defects, Band Alignments, and Fermi Level Pinning

Native Defects



- Cd-rich: Abundant donors
- S-rich: V_{Cd}^{2-} compensating acceptors make n-*type* doping difficult

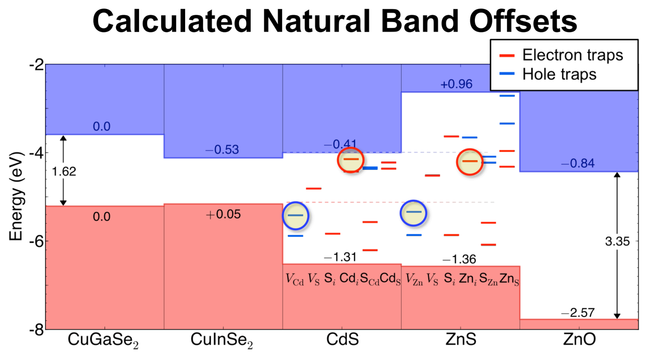
- Zn-rich: V_{Zn}^{2-} very favorable, *n*-type material very difficult
- S-rich: Abundant acceptors, *n*-type unachievable

→ Large conduction band offset of ZnS makes native Zn vacancies favorable, which compensate donors

- CdS has near-ideal ΔCBM wrt CI(G)S
- ZnS CBM too high!
- ZnO CBM too low, but large E_g opened in VBM

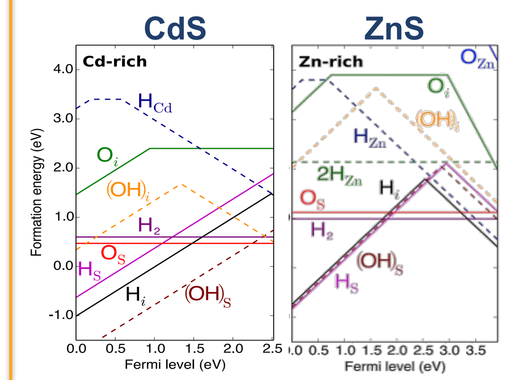
⇒ **(Cd,Zn)(O,S) can be ideal**

Calculated Natural Band Offsets



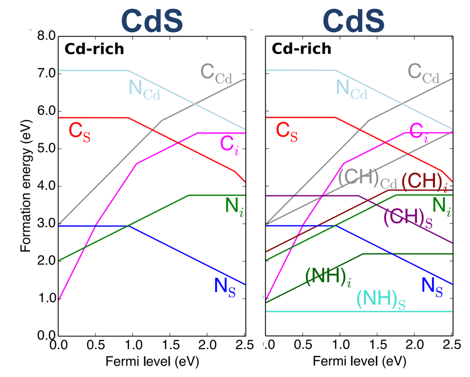
Growth-Related Impurities

O, H, & OH defects (PVD & CBD impurities)



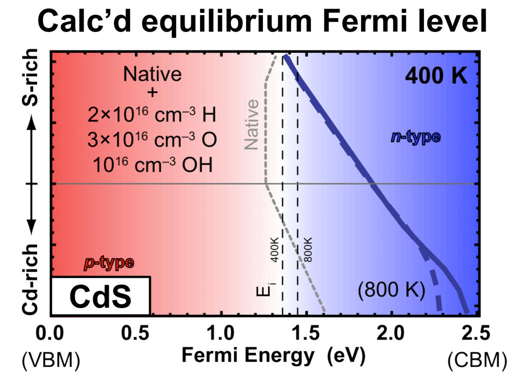
- O, H, OH in CdS are shallow donors → aid *n*-type doping
- In ZnS, these are amphoteric and pin Fermi level more intrinsic

C, N, & complexes w/ H (CBD impurities)

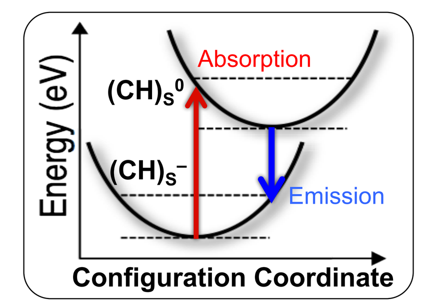


- C, N = deep acceptors in CdS & ZnS
- N is passivated by H, C is not
- ZnS behavior same as CdS

Calc'd equilibrium Fermi level



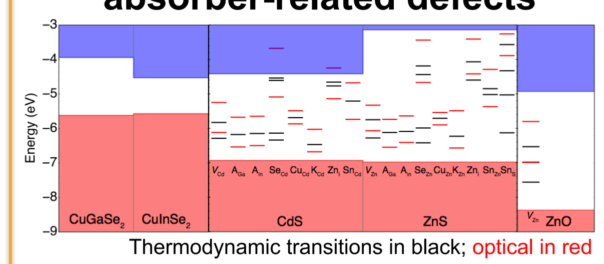
Optical absorption from C-H defects is in the visible



$(CH)_S$ (0/–) : 1.65 eV / 0.40 eV

Intermixing

Deep levels from stable absorber-related defects



CIGS —Diffusion→ CdS

Cu In Ga Se

- Cu: shallow donor; very mobile (fast diffuser)
- Ga, In: shallow donors; not very mobile in CdS
- Se: neutral; immobile

Na & K act similar to Cu:

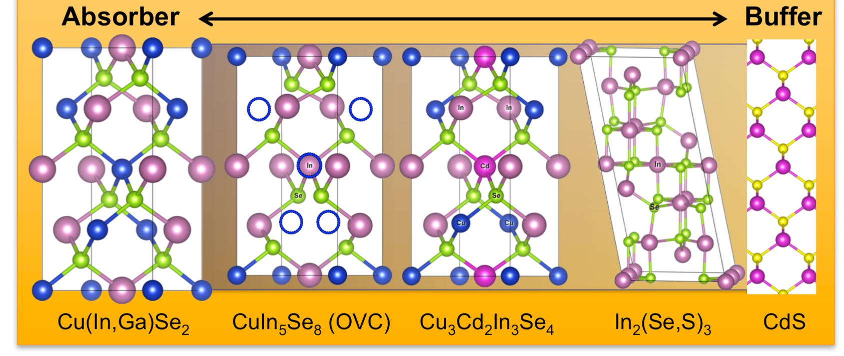
- Donors that can passivate interfacial hole traps from V_{Cd}^{2-}
- Na or K may compensate for Cu deficiency at CIGS/CdS interface

Migration Energy Barriers (eV)

Defect	CdS ∥ c-axis	CdS ⊥ c-axis	ZnS ∥ c-axis	ZnS ⊥ c-axis
V_M^{2-}	1.02	1.02	1.21	1.23
V_S^0	2.44	2.07	2.90	2.49
In_i^+	0.73	0.51	0.66	0.38
Ga_i^+	0.94	0.75	0.95	0.87
Se_i^0	0.40	0.38	0.47	0.33
Cu_i^+	0.64	0.26	0.30	0.23
Zn_i^0	0.69	0.33	0.59	0.44
Zn_i^{2+}	0.64	0.27	0.44	0.32
Sn_i^{2+}	1.13	1.00	1.19	0.92
Na_i^+	0.99	1.09	1.51	1.82
K_i^+	1.51	0.50	1.49	0.45

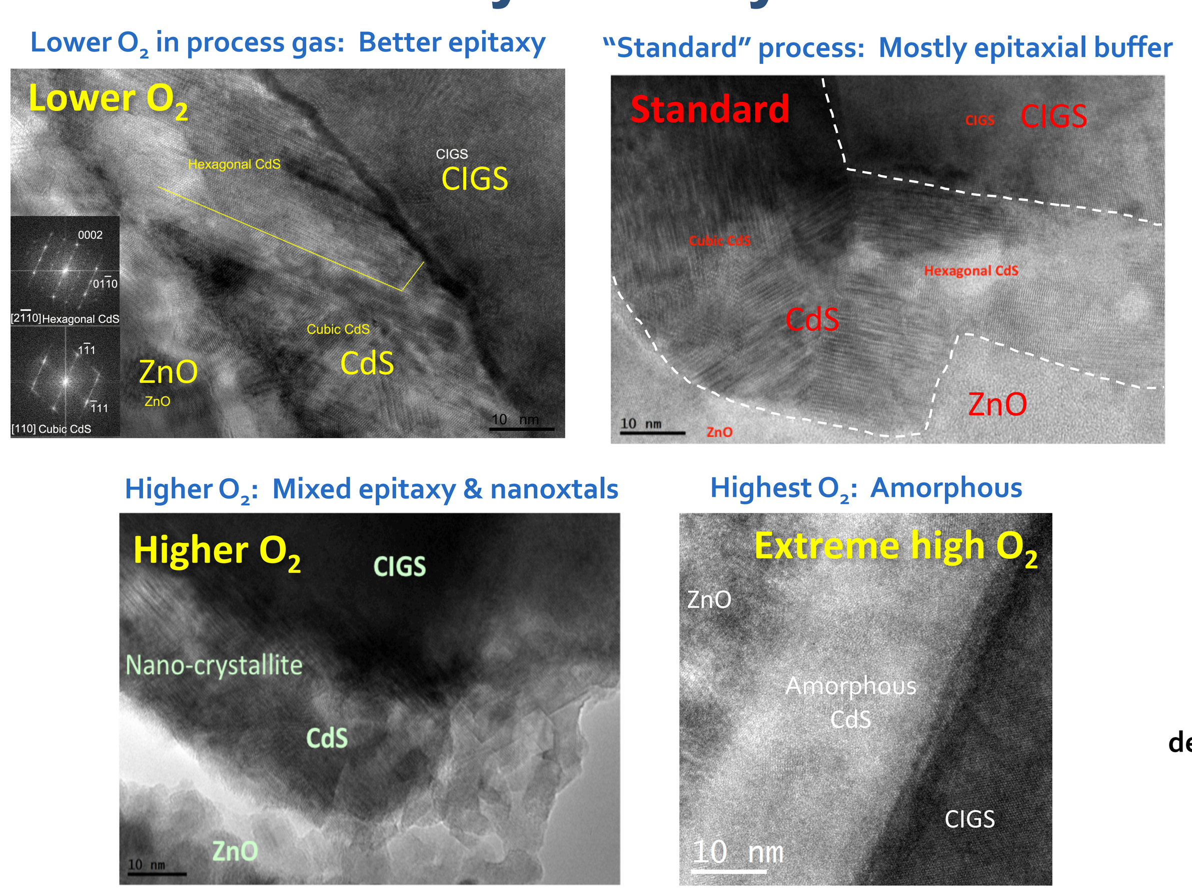
[J.B.Varley & V.L, *J. Appl. Phys.*, in prep (2014).]

Interface also may comprise a number of *interphase* compounds:



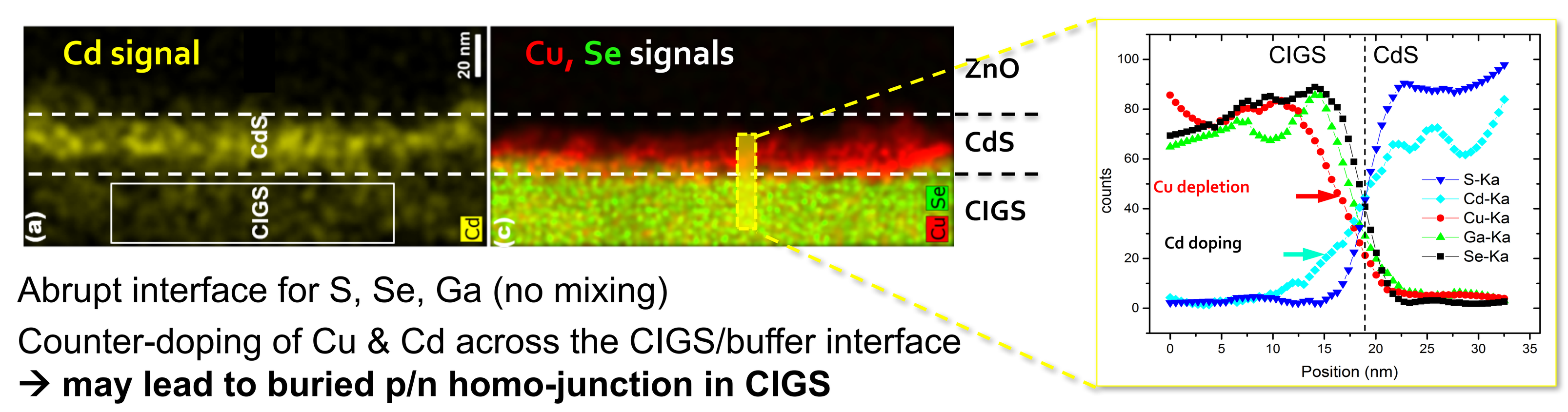
3. Control of Film Deposition Characterized by STEM Imaging and EDS Analysis

Crystallinity



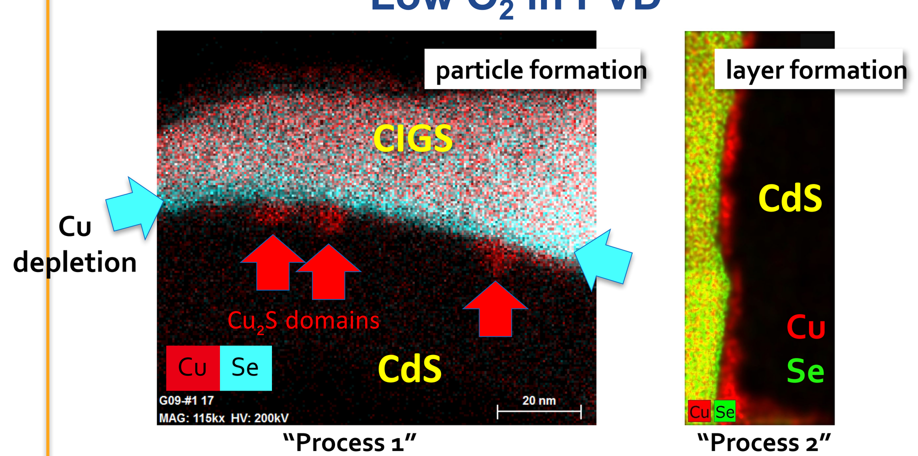
- O_2 in process gas modifies lattice match and crystallinity
- Can achieve epitaxial CdS with PVD sputter process

Heterojunction Intermixing and Secondary Phases



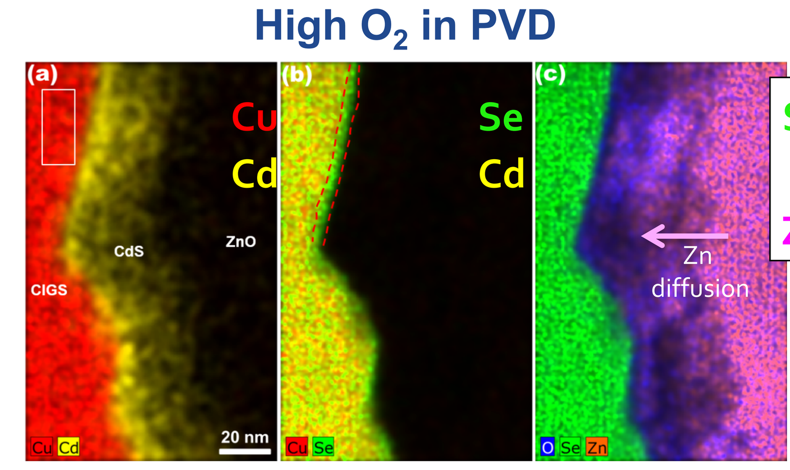
- Abrupt interface for S, Se, Ga (no mixing)
- Counter-doping of Cu & Cd across the CIGS/buffer interface
  → may lead to buried p/n homo-junction in CIGS

Low O_2 in PVD



- Cu-rich phase formation in buffer
- Morphology depends on process conditions

High O_2 in PVD



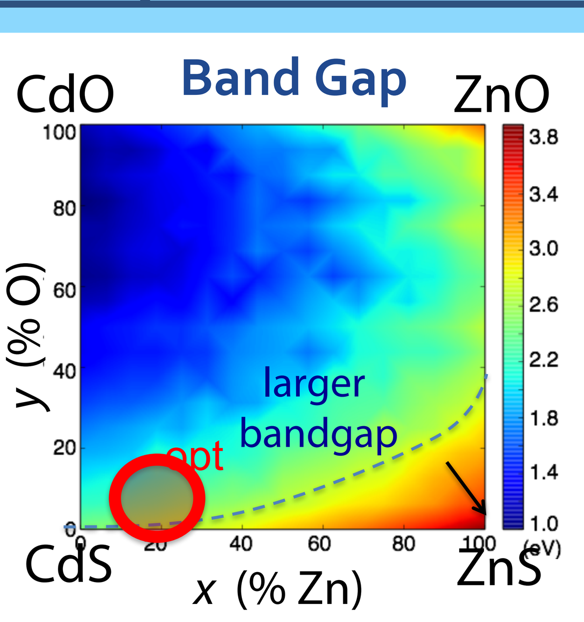
- High oxygen content suppresses Cu diffusion from CIGS, but enhances Zn diffusion from ZnO

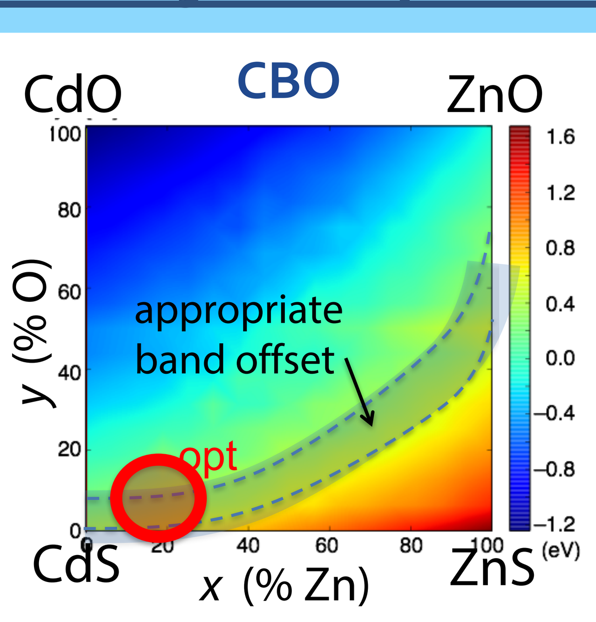
4. Computational Optimization of Alloy Composition for High-Performance Buffer

$(Cd_{1-x}Zn_x)(O_yS_{1-y})$ quaternary provides optimization degrees of freedom

Properties:

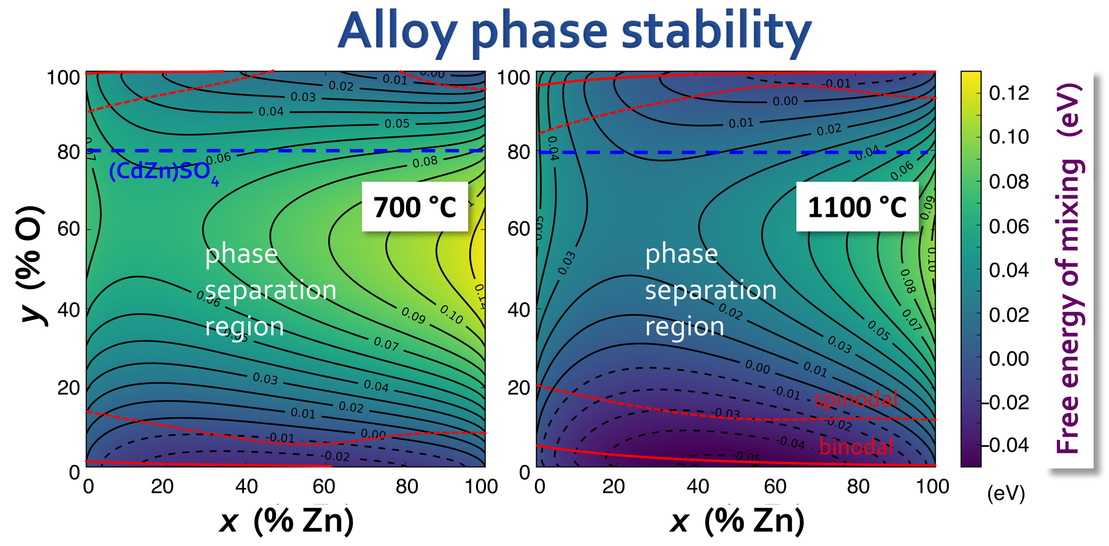
- band gap
- band offset
- lattice match
- dopability





- Targets: $E_g > E_g^{CdS}$; $-0.05 < \Delta CBO < 0.2$ eV; lattice match ±2.5%

Alloy phase stability



- Thermodynamic driving force for phase separation even at high T
- Secondary phases are very stable: e.g. $(Cd,Zn)SO_4$

5. Major Conclusions

- CdS is naturally favorable for its *n*-type dopability and favorable band alignment with CIGS
- ZnS is a BAD wide band gap buffer: ΔE_c too high, hard to *n*-dope, recombination centers from native defects
  ⇒ **But (Cd,Zn)(O,S) is a promising alloy system**
- CIGS/buffer interface properties are critical and complicated
  - Recombination affected by crystallinity
  - Intermixing can bury *p-n* junction (Cd counter-doping)
  - Intermixing can lead to unfavorable secondary phases (Cu in CdS)
  - Sputter deposition conditions, particularly oxygen in process gas, can control quality and composition of interface region
- Careful selection and optimization of buffer material is dependent on absorber material

References:

1. J.B. Varley and **V. Lordi**, "Electrical properties of point defects in CdS and ZnS," *Applied Physics Letters* 103, 102103 (2013).
2. J.B. Varley and **V. Lordi**, "Intermixing at the absorber-buffer layer interface in thin-film solar cells: The electronic effects of point defects in $Cu(In,Ga)(Se,S)_2$ and $Cu_2ZnSn(Se,S)_4$ devices," *Journal of Applied Physics*, 116, 063505 (2014).
3. X.Q. He, G. Brown, K. Demirkan, N. Mackie, **V. Lordi**, A. Rockett, "Microstructural and Chemical Investigation of PVD-CdS/PVD-$CuIn_{1-x}Ga_xSe_2$ Heterojunctions: A Transmission Electron Microscopy Study," *IEEE J. of Photovoltaics*, 4, 1625 (2014).
4. X. He, P. Ercius, J. Bailey, G. Zapalac, N. Mackie, A. Bayman, J. Varley, **V. Lordi**, and A. Rockett, "Cu-rich domains and secondary phase in PVD-CdS/PVD-$CuIn_{1-x}Ga_xSe_2$ heterojunctions," *Proc. 2015 IEEE 42nd Photovoltaic Specialist Conference*, New Orleans, June 14-19 (2015).
5. J.B. Varley, **V. Lordi**, X. He, and A. Rockett, "First principles calculations of point defect diffusion in CdS buffer layers: Implications for $Cu(In,Ga)(Se,S)_2$ and $Cu_2ZnSn(Se,S)_4$-based thin-film photovoltaics," *Journal of Applied Physics* **119**, 025703 (2016).
6. X.Q. He, J.B. Varley, P. Ercius, T. Erikson, J. Bailey, G. Zapalac, D. Poplavskyy, N. Mackie, A. Bayman, **V. Lordi**, and A. Rockett, "Intermixing and Formation of Cu-Rich Secondary Phases at Sputtered $CdS/CuInGaSe_2$ Heterojunctions," *IEEE J. of Photovoltaics* **6**, 1308 (2016).
7. J.B. Varley, X. He, A. Rockett, and **V. Lordi**, "Stability of $Cd_{1-x}Zn_xO_yS_{1-y}$ Quaternary Alloys Assessed with First-Principles Calculations," ACS *Applied Materials & Interfaces* **9**, 5673 (2017).
8. X. He, T. Paulauskas, P. Ercius, J. Varley, J. Bailey, G. Zapalac, D. Poplavskyy, N. Mackie, A. Bayman, R. Klie, **V. Lordi**, A. Rockett, "Cd doping at PVD-CdS/CuInGaSe2 heterojunctions," *Solar Energy Materials and Solar Cells* **164**, 128 (2017).
9. J.B. Varley, **V. Lordi**, X. He, and A. Rockett, "Exploring Cd-Zn-O-S alloys for improved buffer layers in thin-film photovoltaics," *Physical Review Materials* **xx**, xxxx (2017), *in press*.
10. N. Mackie, G. Zapalac, W. Zhang, J. Corson, X. He, A. Rockett, J. Varley, and **V. Lordi**, "Hexagonal Phase Epitaxial Cadmium Sulfide on Copper Indium Gallium Selenide for a Photovoltaic Junction," provisional filed 5/15/2015, US application #62162371; PRC (China) application # 201610319278.4.

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