Ultratech CNT

Atomic Layer Deposition of Chalcogenide Thin Films

PUBLICATION REVIEW ON ULTRATECH ALD SYSTEMS

09.10.2015

Highlights

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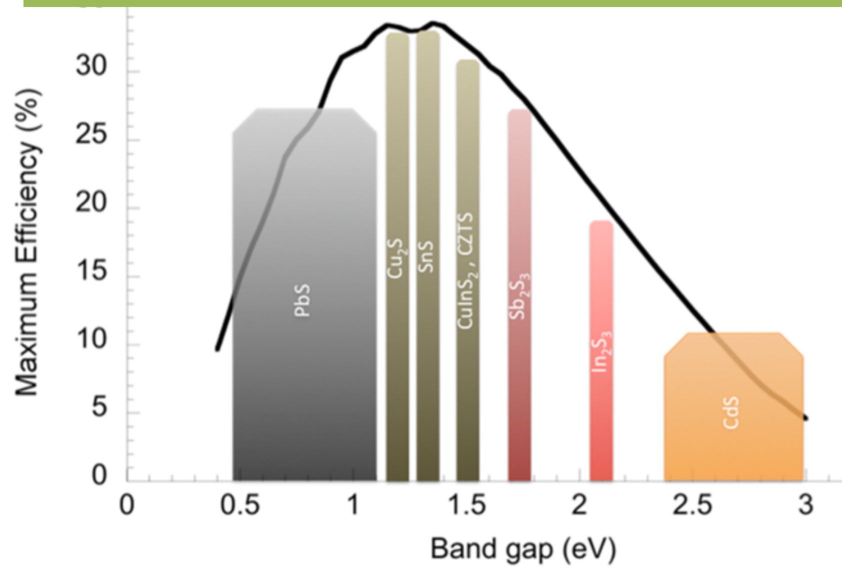
- Benefits of ALD for nano-manufacturing of chalcogenides
- Atomic level thickness control
- Deposition on 3D nanostructures using Expo Mode
- Control of composition in multicomponent sulfides
- Wide range of sulfides deposited by customers:
- Cu_2S, Sb_2S_3, In_2S_3, SnS, ZnS, PbS, Cu_2ZnSnS_4 for PVs
- MoS_2 for 2D materials
- CNT has extensive R&D and manufacturing experience with sulfides, e.g., Zn(O,S) and handling of H_2S
- Key users: Argonne National Lab, Stanford U., U. of Hamburg, U. of Michigan

Introduction

- Great interest in sulfides for photovoltaics, photonics, catalysis
- Requires H_2S
- Chalcogenide photovoltaics
  - Absorber
    - band gaps and energy levels more suitable than oxides
    - 31-34% efficiency at 1-1.6eV
    - CZTS quaternary synthesized for first time
    - Cu_2S stabilized by thin ALD oxides
  - Buffer / Emitter
    - In_2S_3, ZnS, and CdS, and Zn(O,S)
- Energy Storage
  - Cu_2S / CNT cathodes @260 mA h g^{-1}
  - Li_2S @ 800 mA h g^{-1}
- Photonics
  - ZnS for TFEL displays (first ALD industrial application)

1. Dasgupta, N. P., et al., Accounts Chem Res 48, 341–348 (2015).

Single junction efficiency limits



ALD sulfide absorbers

sulfide	band gap (eV)	majority carrier	type	power eff. (%)	record eff. (%)[34]	ref(s)
$CuInS_2$	1.5	p-type	ETA	4	12	35
CZTS	1.5	p-type	thin film	–	12.6	21
Cu_xS	1.2	p-type	ETA	<0.1	10	36
SnS	**1.3**	**p-type**	**thin film**	4	4	37, 38
PbS	0.4	p-type	QDSSC	0.6	6	39
Sb_2S_3	1.7	p-type	thin film	5.8	8	40
CdS	2.4	n-type	QDSSC	0.3	3	41
In_2S_3	2.1	n-type	ETA	0.4	3	42

[a]**Bold** denotes record power efficiency for any deposition method. ETA = extremely thin absorber. QDSSC = quantum-dot-sensitized solar cell.

CIGS - Photovoltaics

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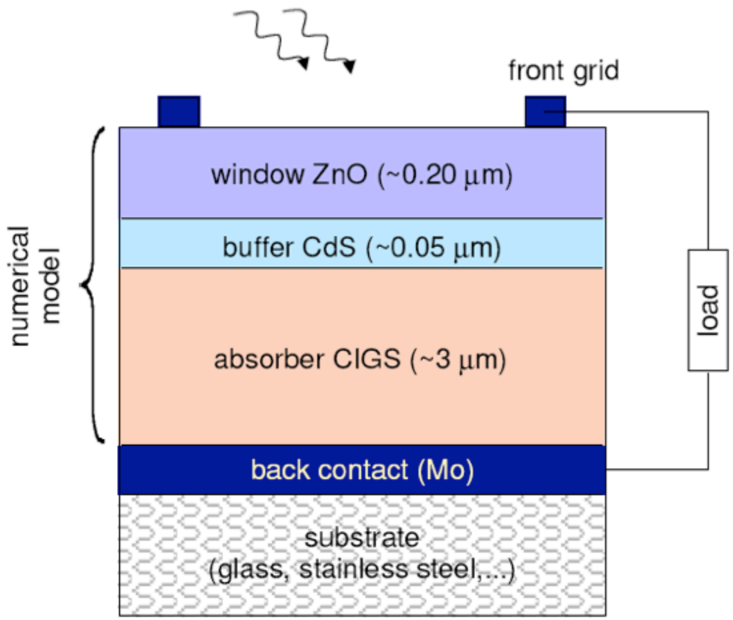

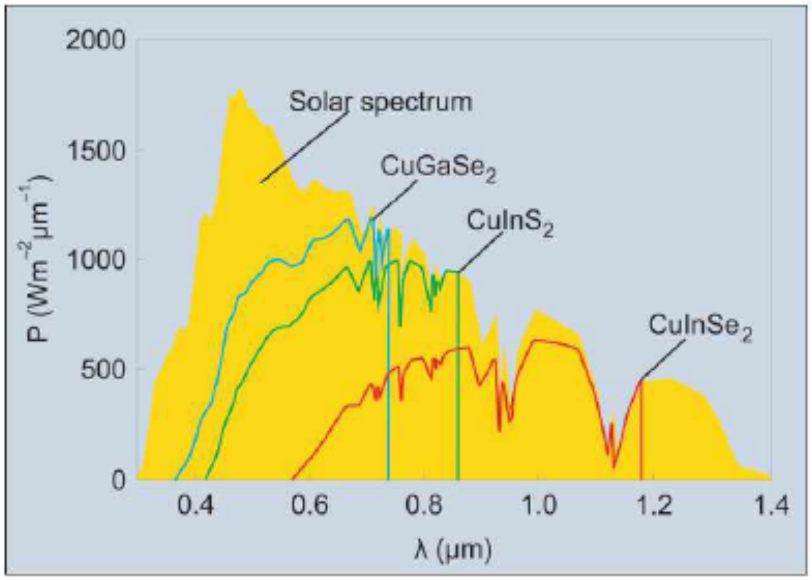

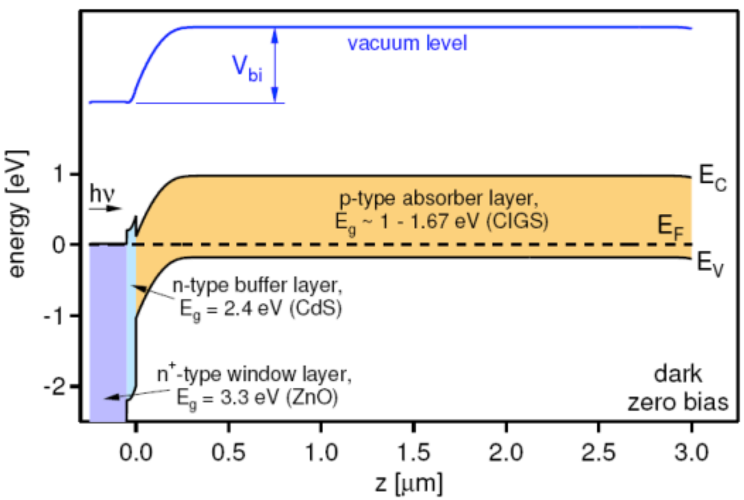

- ❑ Absorber / buffer / TCO combination determines spectral capture range
- ❑ Max efficiency to date at 20%
- ❑ Complex heterojunction, where buffer and absorber interface determine band bending and ultimate efficiency
- ❑ Buffer material, composition, optical properties, and film uniformity are crucial

$ZnO_{(1-x)}S_x$ composition

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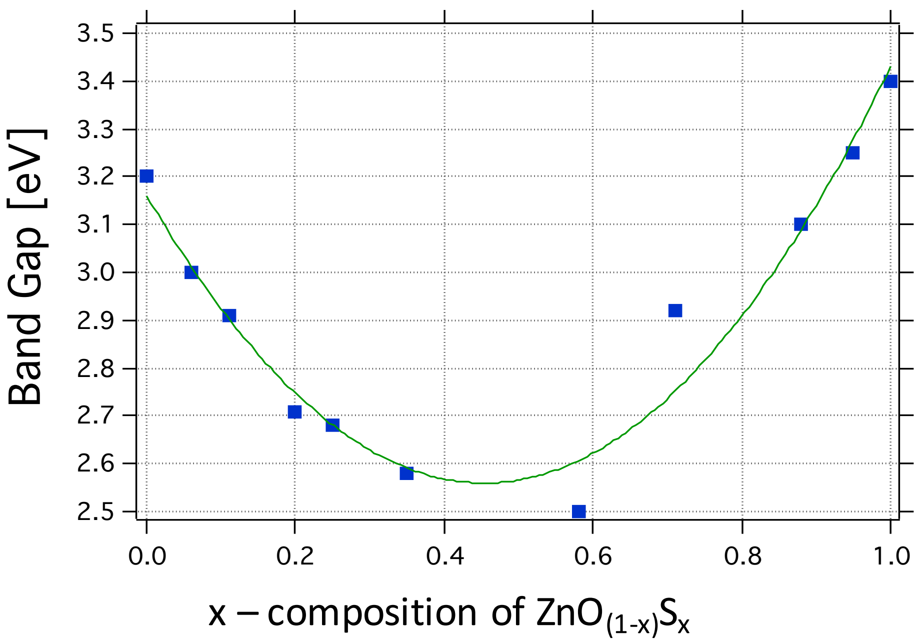
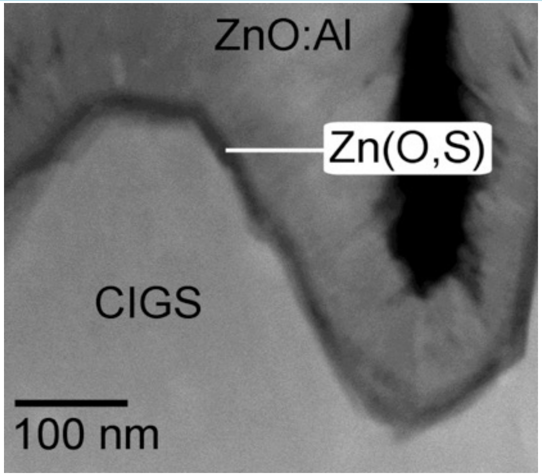
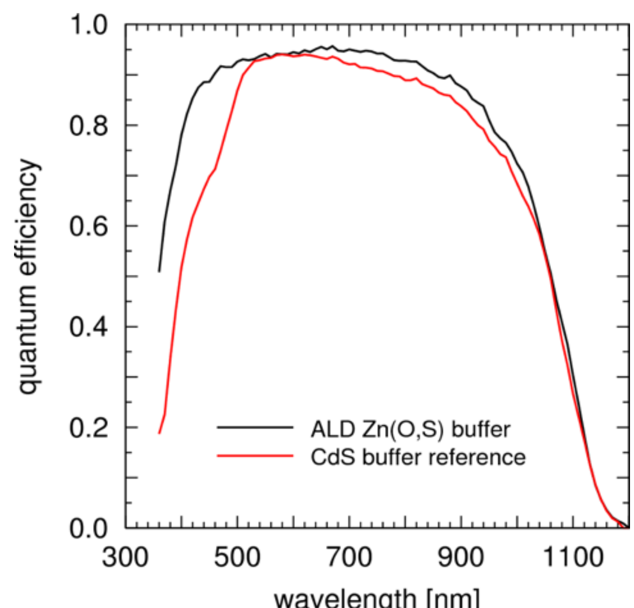
Composition controlled by changing the number of ZnS /ZnO cycles in order to match given CIGS composition



TEM cross-section of a CIGS cell with ALD grown Zn(O,S) buffer layer.



Quantum efficiency measurement



1. Bhargava et.al., Journal of the Korean Physical Society, Vol53, No. 5,, 2008.
2. Zimmermann U.,et al., 21st Eur. Photovoltaic Solar Energy Conference (2006), Dresden

Cu_2ZnSnS_4 (CZST)

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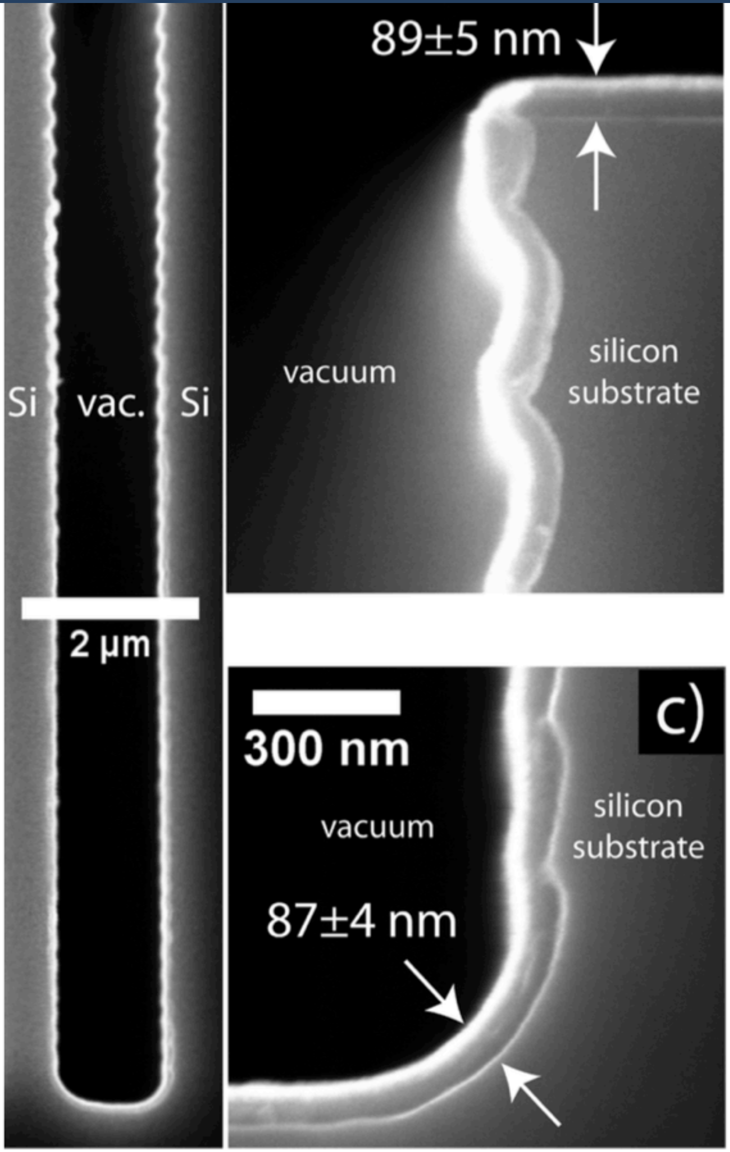
- Objectives
  - Low cost seminconductor (CZST) for photovoltaic
  - 1.4 eV band gap, conformality in 3D
  - Compositional control of quaternary materials
- Experimental
  - Savannah S200, Expo, H_2S kit, 150˚C
  - Cu_2S: Cu_2DBA (Strem) @ 160˚C + 1% H_2S
  - SnS: TDMASn + 1% H_2S
  - ZnS: DEZ + 1% H_2S
  - 2 strategies: trilayers and nanolaminates

Cu_2S / SnS_2 / ZnS trilayer deposited on a silicon trench wafer



Thimsen et al. , Chemistry of Materials, 24(16), 3188–3196 (2012). doi:10.1021/cm3015

Interface and composition profile in CZST

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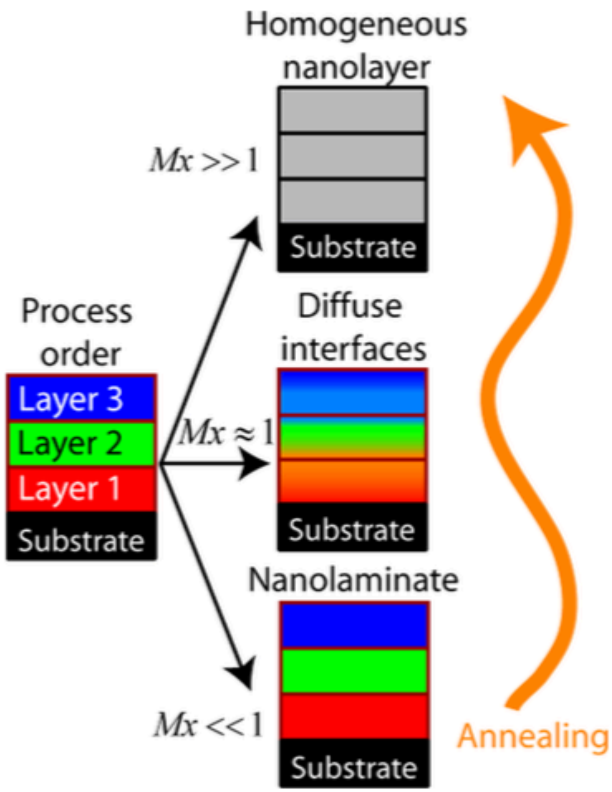
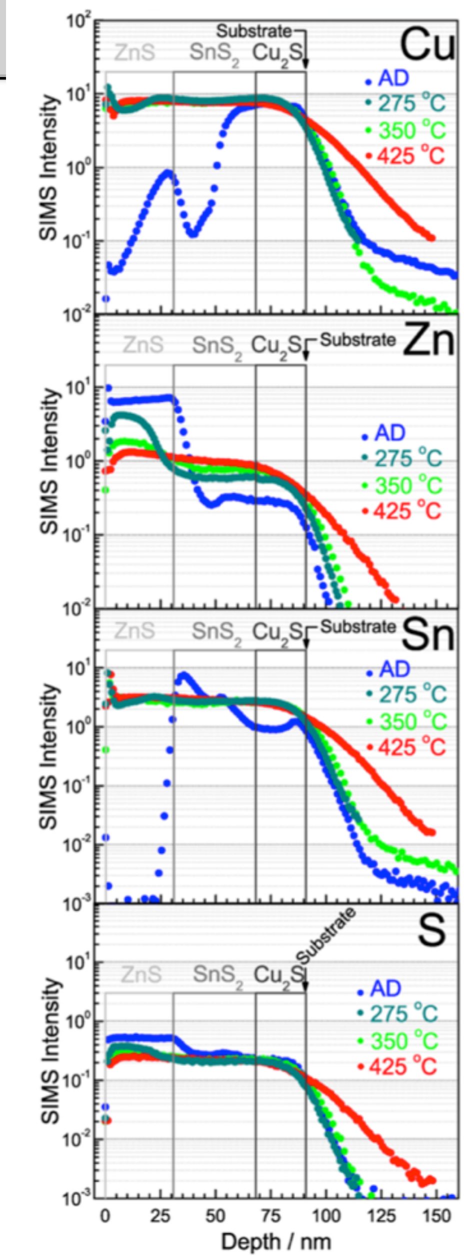
1. Thimsen, Chemistry of Materials, 24(16), 3188–3196 (2013) [Argonne]





Cu_2S cathode for LIB

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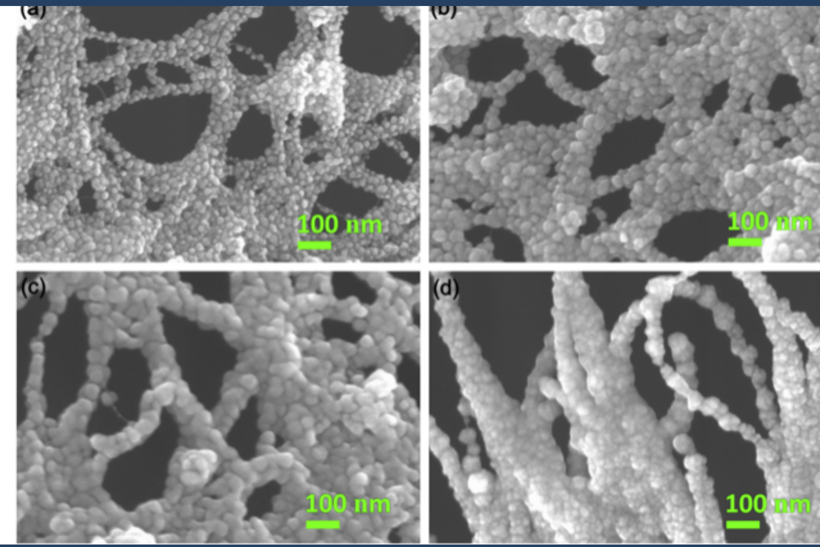
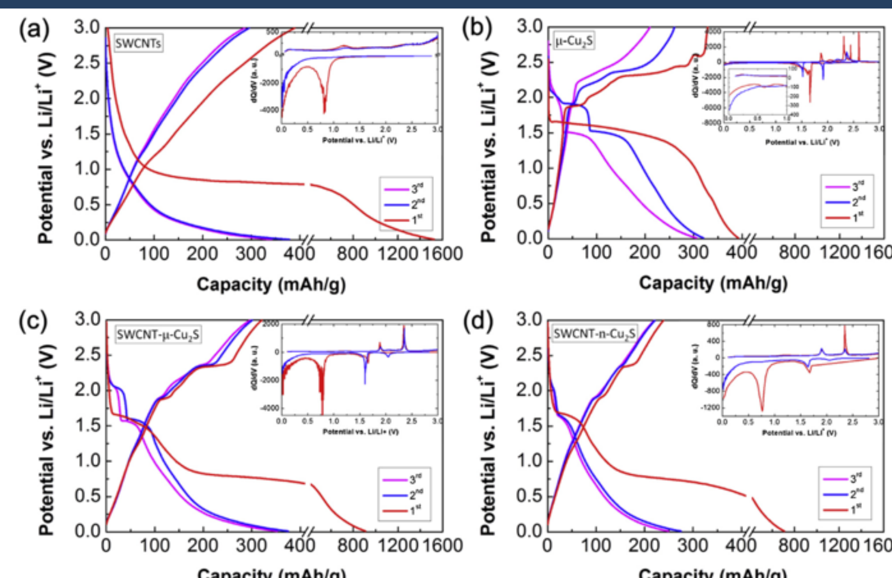
1 Meng, X., Journal of Power Sources, 2015, 280, 621–629 [Argonne NL]

- ❑ Objectives
  - Cu_2S deposited on single wall carbon nanotubes
- ❑ Experimental
  - Savannah S200 at 135˚C, expo mode
  - CuAMD (150˚C) and 1% H_2S
  - SWCNT functionalized with 9min O_3
- ❑ Results
  - Core-shell SWCNT-n-Cu_2S exhibits high charge discharge/stability
  - high capacity (260mA/g)
  - >99% Coulombic efficiency

Cu_2S on SWCNT (100, 200, 400, 600 cycles)



Charge/discharge for first 3 cycles at 1000 mA/g

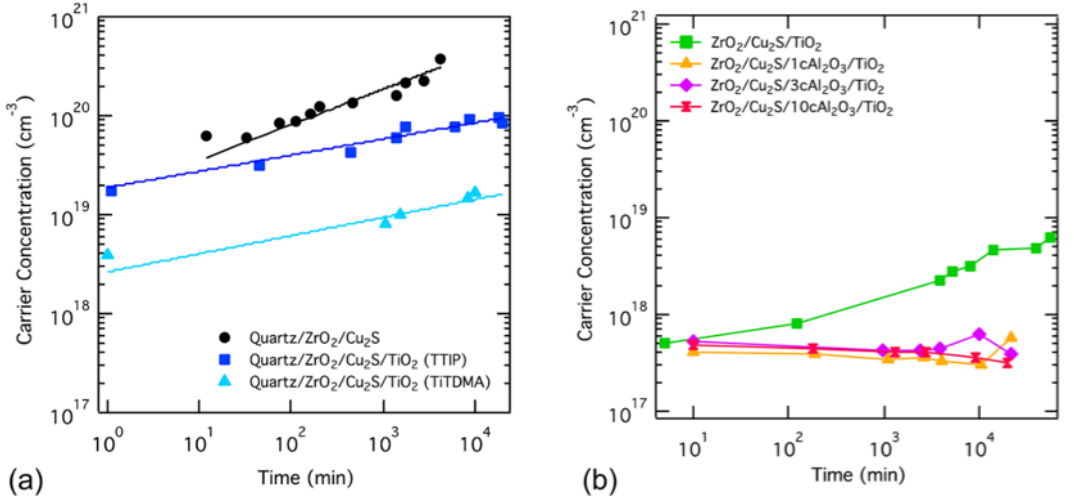


Stabilization of Cu_2S for PVs

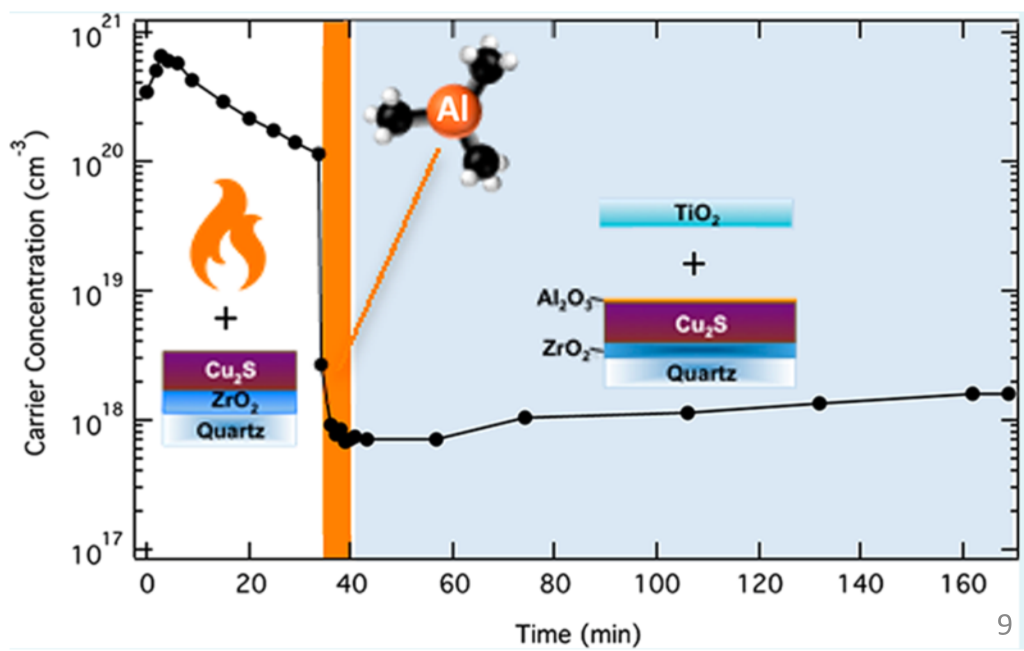
1 . Riha, S. C. et al Acs Appl Mater Inter 131010083550003 (2013). [Argonne NL]

- Cu_2S PV absorber
  - abundant, non toxic, absorption >1E4cm^{-1}
- Issue with Cu_2S/CdS junction due to Cu diffusion
- S200 for Cu_2S from CuAMD/H_2S @145˚C
- TiO_2 ALD used as Cu diffusion barrier and n-type emitter to replace CdS
- 1-2 Al_2O_3 cycles reduce carrier concentration and stabilize film for >2 weeks

Passivation of Cu_2S with TiO_2 & Al_2O_3/TiO_2



Carrier concentration from in-situ IV



In_2S_3 ALD

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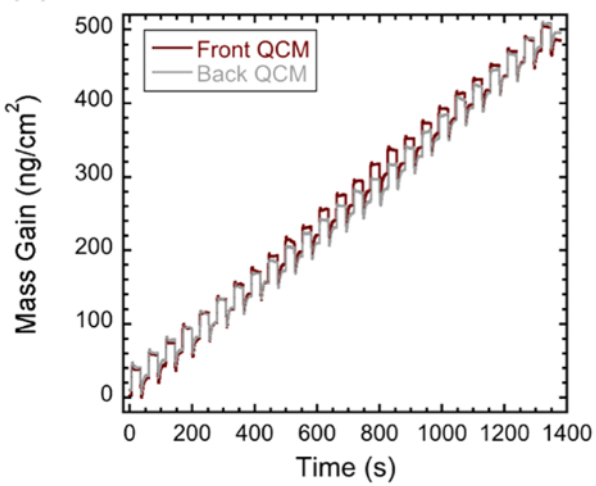
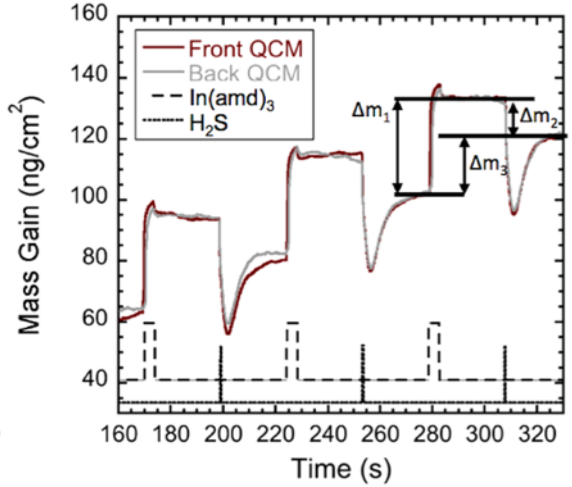
1 McCarthy, R. F., et al, Acs Appl Mater Inter 6, 12137–12145 (2014). [Argonne NL]

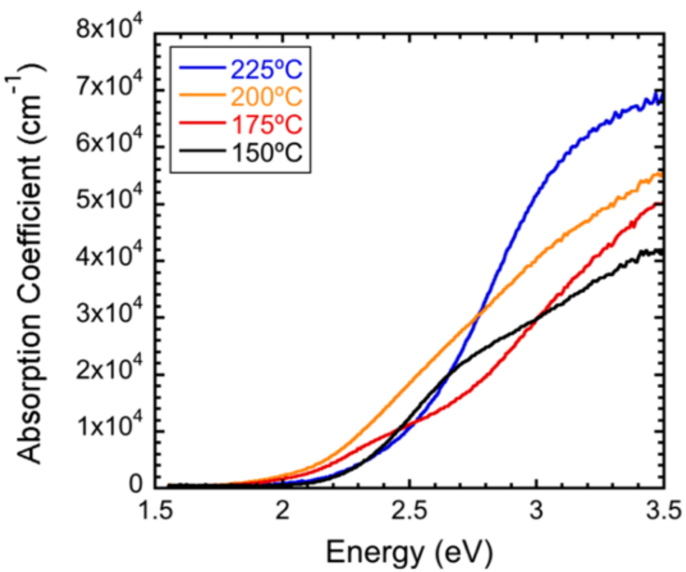
- Chalcogenide PV to replace CdS
- $In(amd)_3$ and H_2S in S200
- Self-limited ALD up to 225˚C
- 0.89Å / cycle @ 150˚C
- No detectable C, N, O halogen (RBS/AES)

Mass Gain during $In(amd)_3$ / H_2S cycles

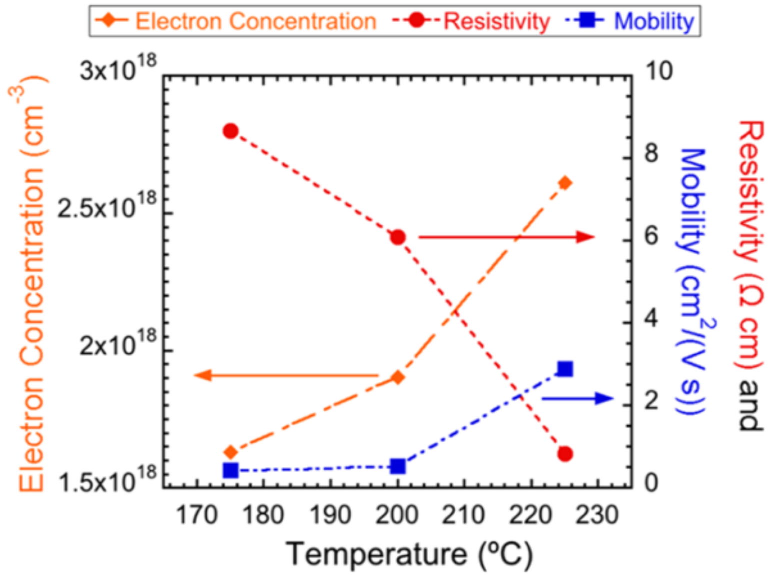




Absorption coefficient at varying dep. temperatures



Impact of process temperature on n-type In_2S_3



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Sulfide work done on Ultratech CNT ALD systems

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2. McCarthy, R. F., Schaller, R. D., Gosztola, D. J., Wiederrecht, G. P. & Martinson, A. B. F. Photoexcited Carrier Dynamics of In2S3 Thin Films. *J. Phys. Chem. Lett.* (2015). doi:10.1021/acs.jpclett.5b00935
3. Baryshev, S. V., Riha, S. C. & Zinovev, A. V. Solar Absorber Cu2ZnSnS4 and its Parent Multilayers ZnS/SnS2/Cu2S Synthesized by Atomic Layer Deposition and Analyzed by X-ray Photoelectron Spectroscopy. *Surf. Sci. Spectra* **22,** 81–99 (2015).
4. Riha, S. C., Schaller, R. D., Gosztola, D. J., Wiederrecht, G. P. & Martinson, A. B. F. Photoexcited Carrier Dynamics of Cu 2S Thin Films. *J. Phys. Chem. Lett.* **5,** 4055–4061 (2014).
5. Sutherland, B. R. *et al.* Perovskite Thin Films via Atomic Layer Deposition. *Advanced Materials* n/a–n/a (2014). doi:10.1002/adma.201403965
6. McCarthy, R. F., Weimer, M. S., Emery, J. D., Hock, A. S. & Martinson, A. B. F. Oxygen-Free Atomic Layer Deposition of Indium Sulfide. *Acs Appl Mater Inter* **6,** 12137–12145 (2014).
7. Riha, S. C. *et al.* Stabilizing Cu 2S for Photovoltaics One Atomic Layer at a Time. *Acs Appl Mater Inter* 131010083550003 (2013). doi:10.1021/am403225e
8. Thimsen, E. *et al.* Interfaces and Composition Profiles in Metal–Sulfide Nanolayers Synthesized by Atomic Layer Deposition. *Chem Mater* **25,** 313–319 (2013).
9. Thimsen, E. *et al.* Atomic Layer Deposition of the Quaternary Chalcogenide Cu 2ZnSnS 4. *Chem Mater* **24,** 3188–3196 (2012).
10. Yang, R. B. *et al.* Pulsed Vapor-Liquid-Solid Growth of Antimony Selenide and Antimony Sulfide Nanowires. *Advanced Materials* **21,** 3170–3174 (2009).
11. Dasgupta, N. P., Walch, S. P. & Prinz, F. Fabrication and Characterization of Lead Sulfide Thin Films by Atomic Layer Deposition. *ECS Transactions* **16,** 29–36 (2008).