Karlsruhe Institute of Technology

Federal Ministry for Economic Affairs and Energy

Laboratory for Electron Microscopy

TEM study of annealing effects on chemical and structural properties of solution-processed Zn(O,S) buffer layers in $Cu(In,Ga)Se_2$ solar cells

X. Jin [a], R. Schneider [a], R. Popescu [a], J. Seeger [b], J. Grutke [b], B. Zerulla [b], H. Kalt [b], M. Hetterich [b,c], D. Hariskos [d], W. Witte [d], M. Powalla [d], D. Gerthsen [a]

[a] *Laboratory for Electron Microscopy, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*

[b] *Institute of Applied Physics (APH), KIT, Karlsruhe, Germany*

[c] *Light Technology Institute (LTI), KIT, Karlsruhe, Germany*

[d] *Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), Stuttgart, Germany*

xiaowei.jin@kit.edu

Outline

1. **Motivation**
2. **Experimental**
3. **Chemical properties of the as-grown & annealed Zn(O,S) buffers**
4. **Bandgap energies of the Zn(O,S) buffers before & after annealing**
5. **Crystal structure of the Zn(O,S) buffers and corresponding phase analyses**
6. **Conclusions**

Motivation

Karlsruhe Institute of Technology

Zn(O,S)

- non-toxic
- wide & tunable bandgap (2.6 - 3.6 eV) [1]
- $Cu(In,Ga)Se_2$ (CIGS) solar cells with solution-processed Zn(O,S) show high conversion efficiency above 23% [2]
- earth abundant, low cost, …

➔ promising buffer material to replace CdS

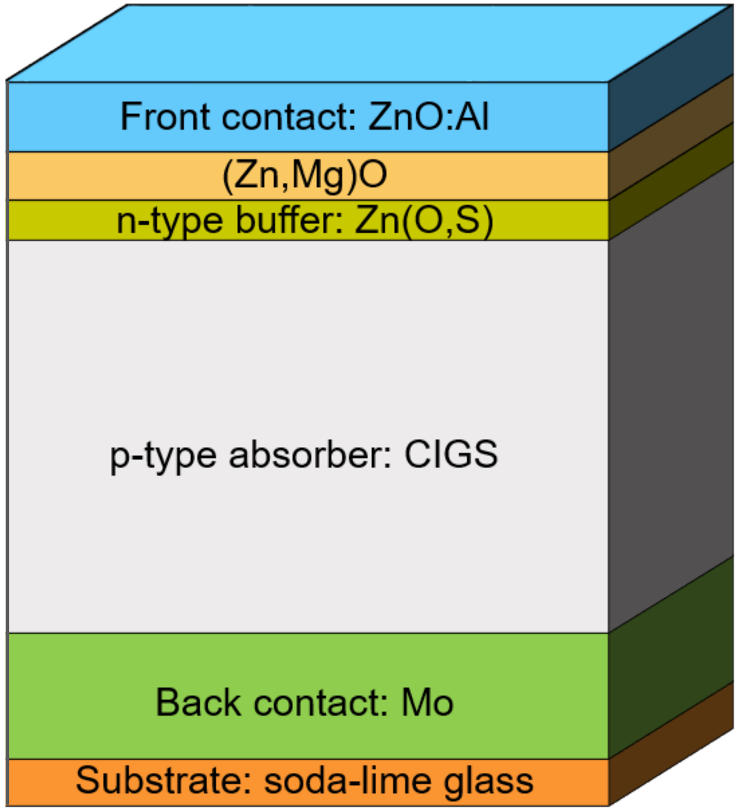
Post-growth annealing

- influences achieved performance

Transmission electron microscopy

- characterize chemical & structural properties

➔ study influence of annealing on microchemistry & microstructure

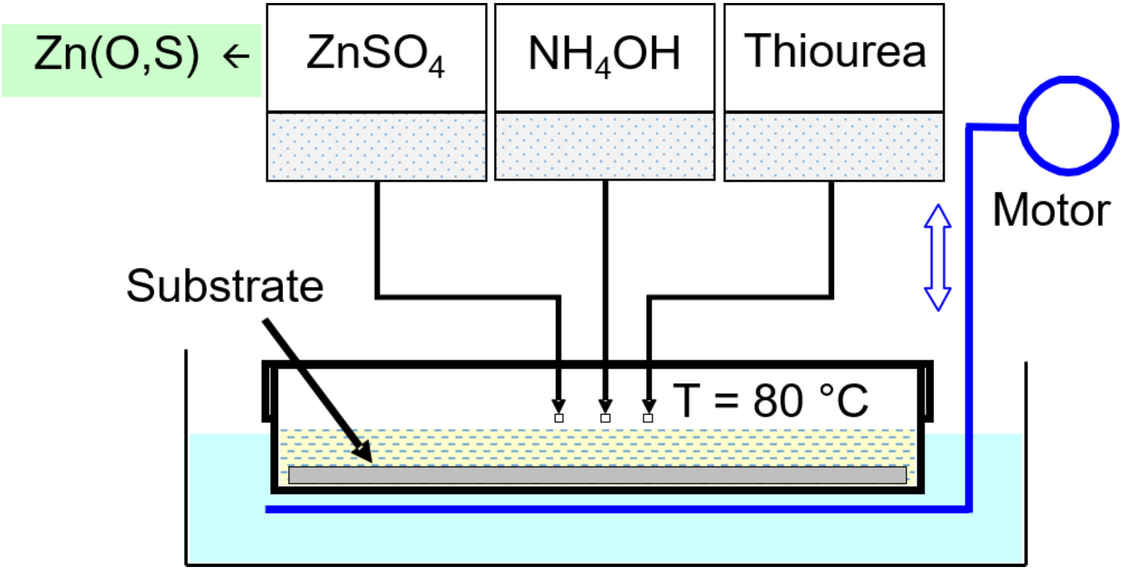


[1] B.K. Meyer *et al*., Appl. Phys. Lett. **85** (2004) 4929
[2] M. Nakamura *et al*., IEEE J. Photovolt. **9** (2019) 1863

Experimental

Fabrication of solar cells

- CIGS: in-line multi-stage coevaporation
- Zn(O,S): chemical bath deposition (CBD), 20 nm
- (Zn,Mg)O: rf-sputtering
- ZnO:Al: dc-sputtering



Annealing

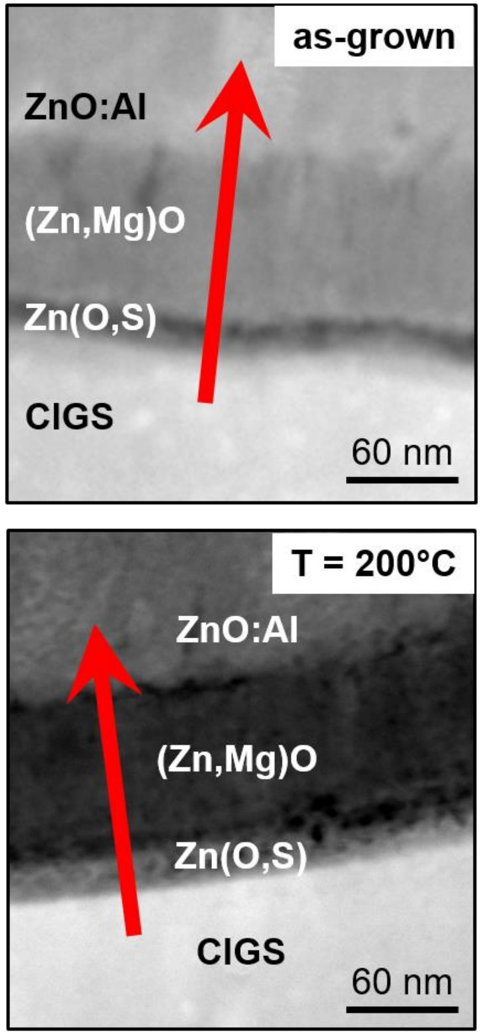
- performed in air on a hot plate, 30 min
- first @ 150˚C, then @ 200˚C

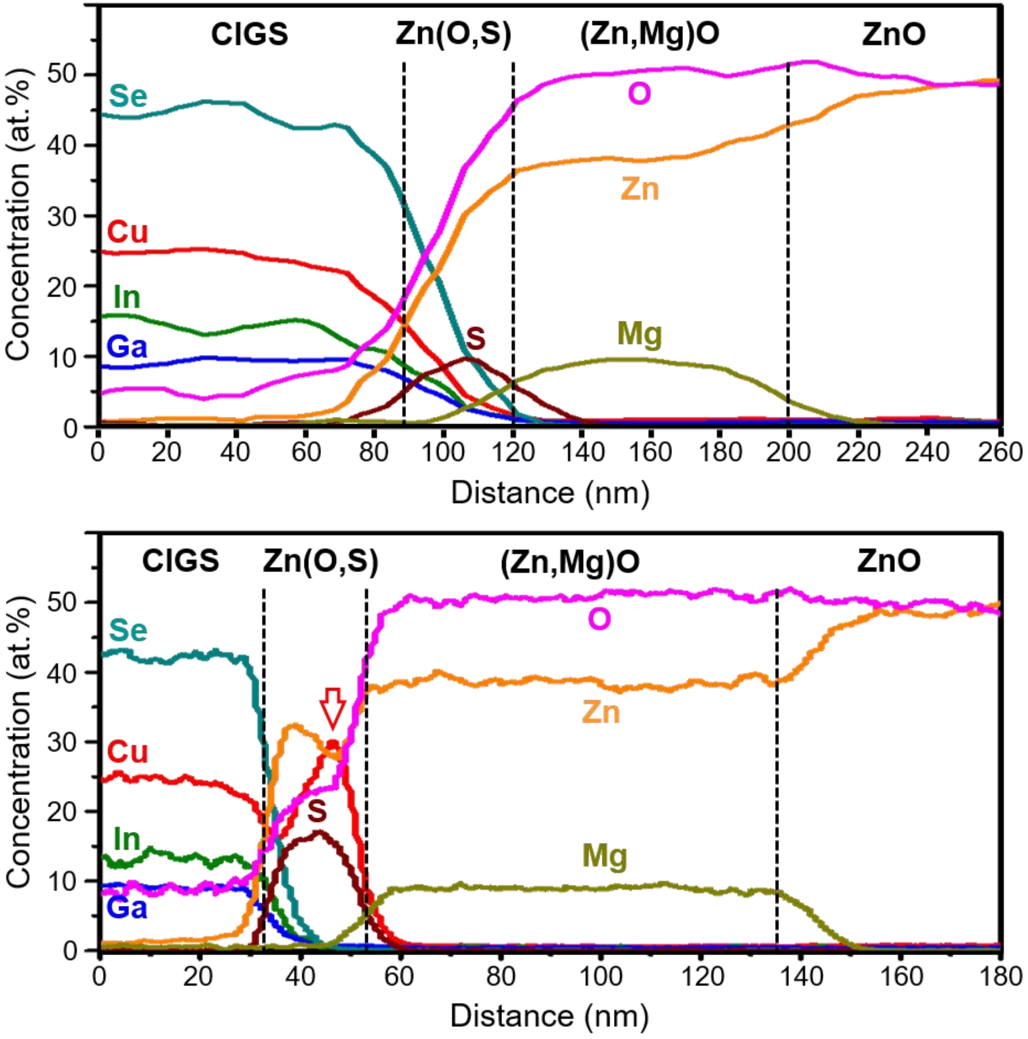
Characterization and phase analysis

- bandgap measurements: angle-resolved electroreflectance spectroscopy (ARER)
- chemical analysis: energy-dispersive X-ray spectroscopy combined with scanning transmission electron microscopy (STEM/EDXS)
- crystal structure: high-resolution transmission electron microscopy (HRTEM) and nanobeam electron diffraction (NBD)

Chemical properties of the Zn(O,S) buffers

Karlsruhe Institute of Technology

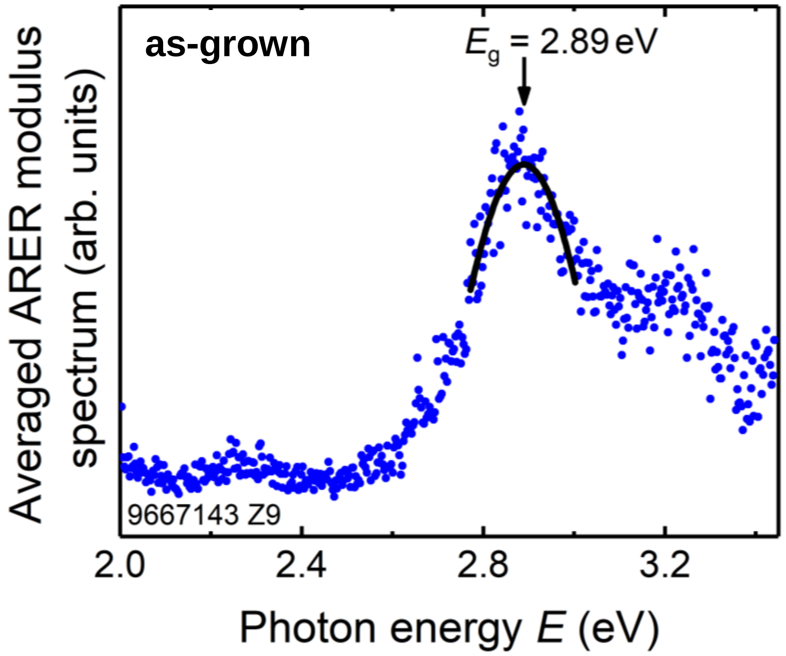


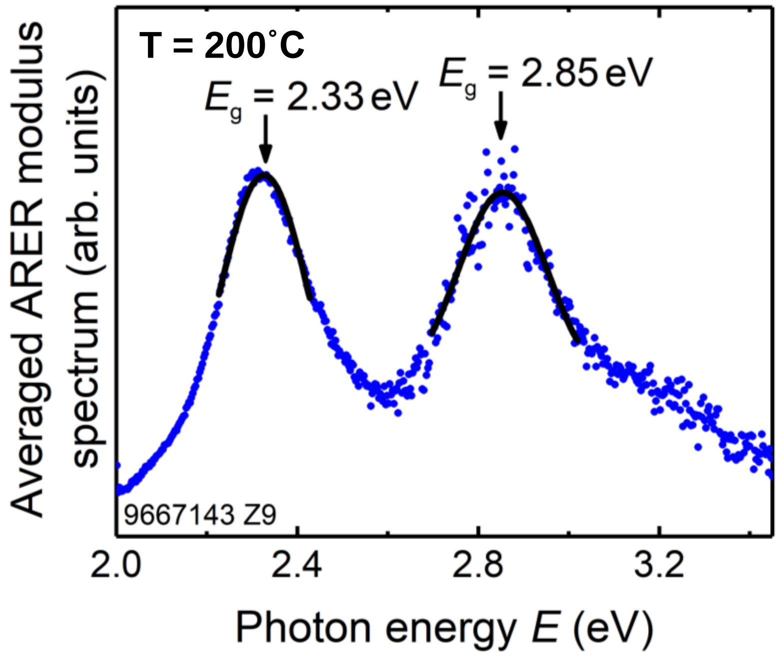


- In as-grown Zn(O,S) buffer, only Zn, O & S present, more O than S; other elements are artifacts
- In annealed Zn(O,S) buffer, the Cu concentration significantly increases, while the Zn concentration decreases
  ➔ interdiffusion of Cu and Zn
- SSO* value increases after annealing

*SSO: [S]/([S]+[O])

Bandgap energies of the Zn(O,S) buffers

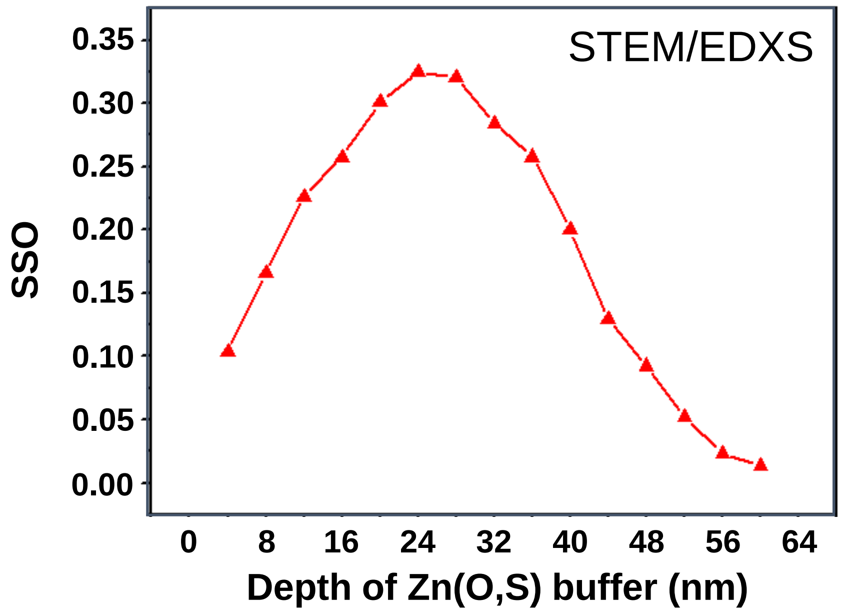


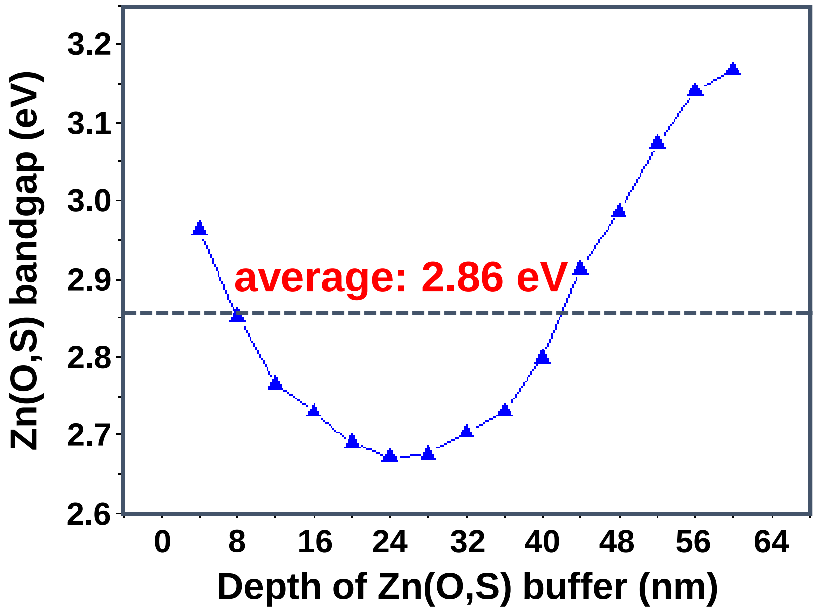


- Before annealing, one resonance at 2.89 eV is detected ➔ bandgap energy of Zn(O,S) (2.6 - 3.6 eV)
- After annealing at 200˚C for 30 min, bandgap of Zn(O,S) slightly changes (2.89 eV ➔ 2.85 eV)
- An additional resonance at 2.33 eV ➔ a secondary phase in the buffer ➔ CuS (2.36 eV), Cu_2Se (2.23 eV), or Cu_3Se_2 (2.37 eV)

J. Seeger *et al.*, IEEE 46th PVSC, USA (2019) 0949
J. Seeger *et al.*, Appl. Phys. Lett. 115 (2019) 263901

Bandgap energies of the Zn(O,S) buffers



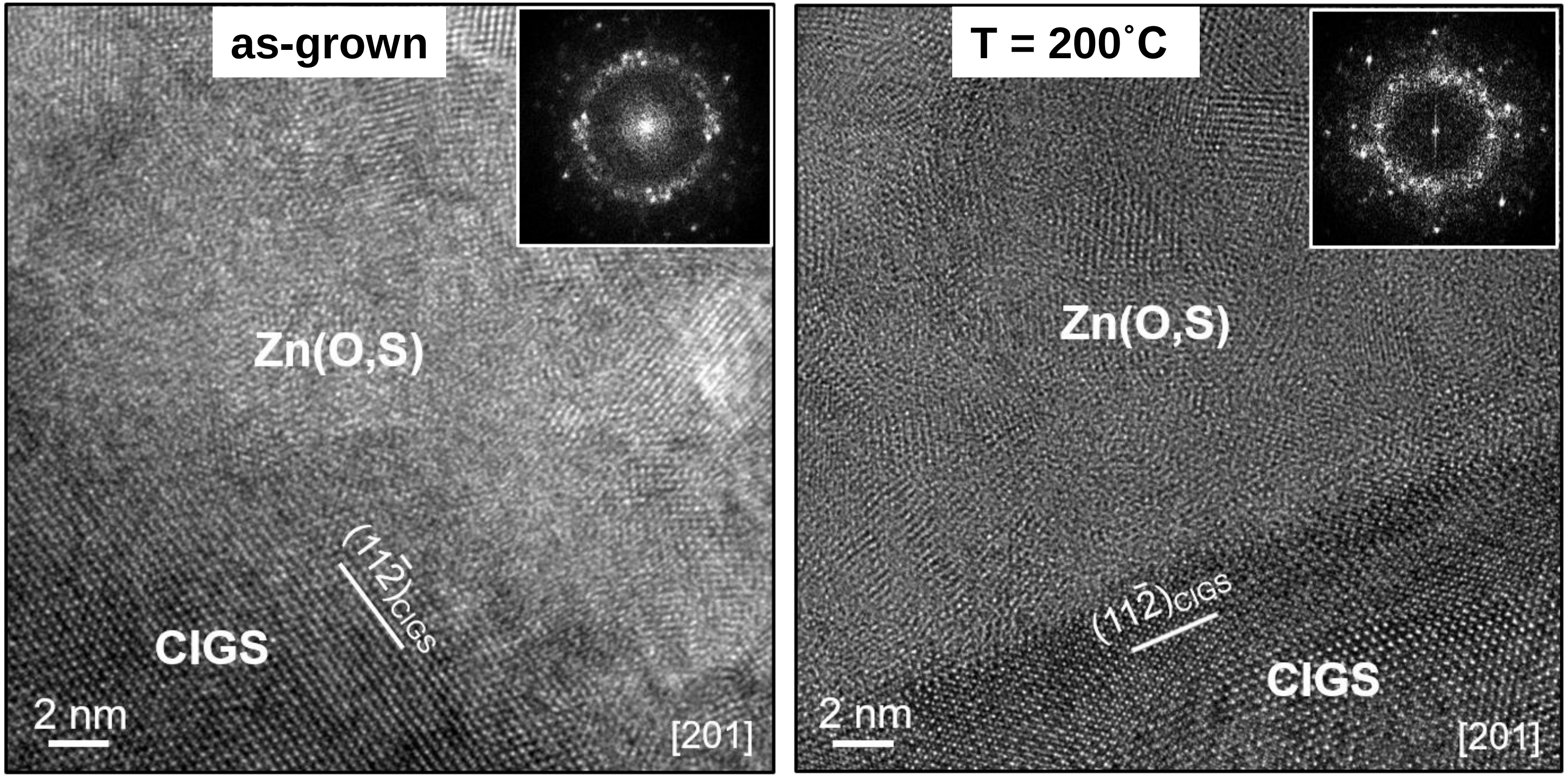


- $\boldsymbol{E_{Zn(O,S)}(x) = x\, E_{ZnS} + (1-x)E_{ZnO} - b(1-x)x}$ [1]
  - $E_{Zn(O,S)}(x)$: bandgap of Zn(O,S)
  - E_{ZnS}: bandgap of ZnS (3.6 eV)
  - E_{ZnO}: bandgap of ZnO (3.2 eV)
  - x: SSO value in Zn(O,S)
  - b: a bowing parameter (~ 3.0 eV)

- Average calculated bandgap 2.86 eV from STEM/EDXS results and the measured bandgap 2.89 eV by ARER match each other
  ➔ reliability of STEM/EDXS and ARER measurements

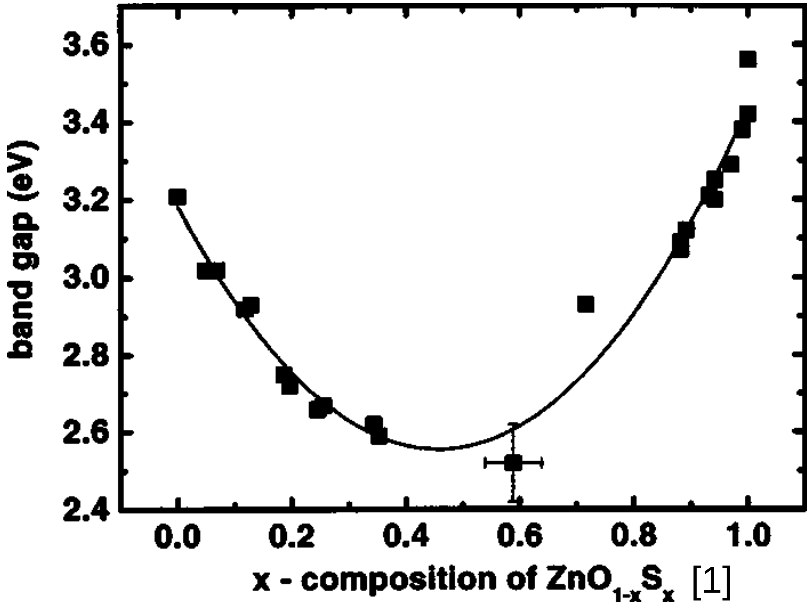
[1] B.K. Meyer *et al.*, Appl. Phys. Lett. **85** (2004) 4929

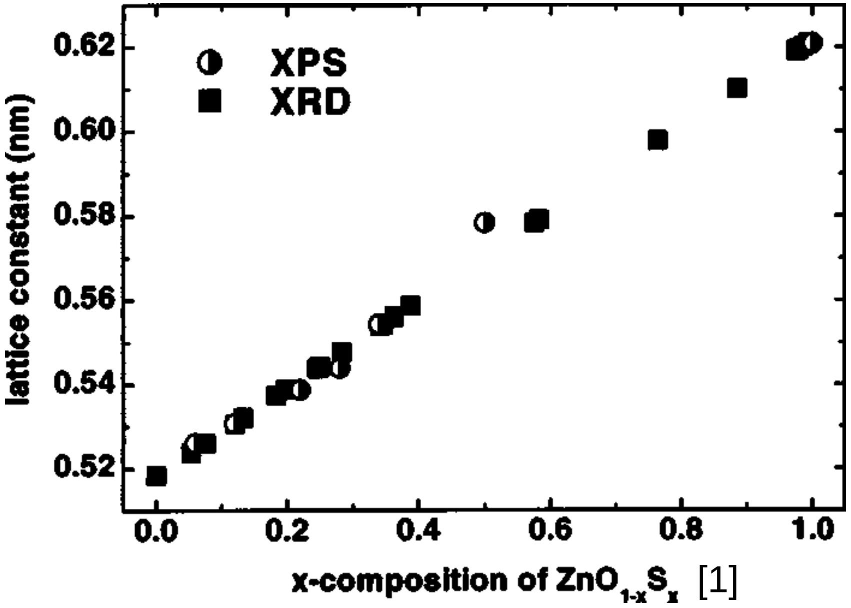
Crystal structure of the Zn(O,S) buffers



- Nanocrystalline structure of the Zn(O,S) buffer layer, independent of the orientation of the underlying CIGS grains
- Annealing @ 200˚C does not significantly change the crystallinity of the buffer layer
- Detailed analysis of chemical phases within Zn(O,S) buffer layers would be performed by NBD

Phase analyses of the Zn(O,S) buffers





$E_{Zn(O,S)}(x) = x\,E_{ZnS} + (1-x)E_{ZnO} - b(1-x)x$

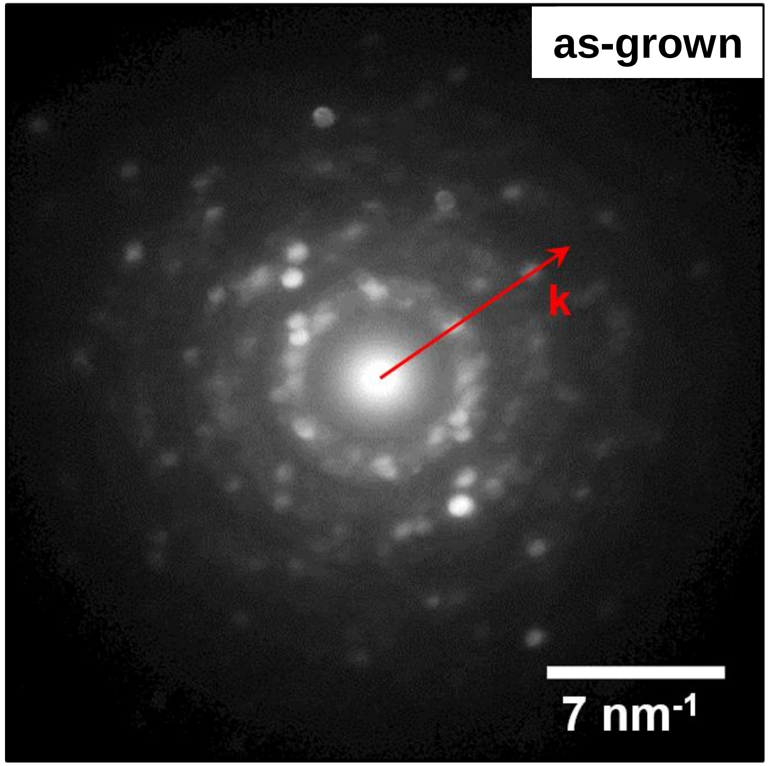
Lattice constant = $0.1x + 0.52$

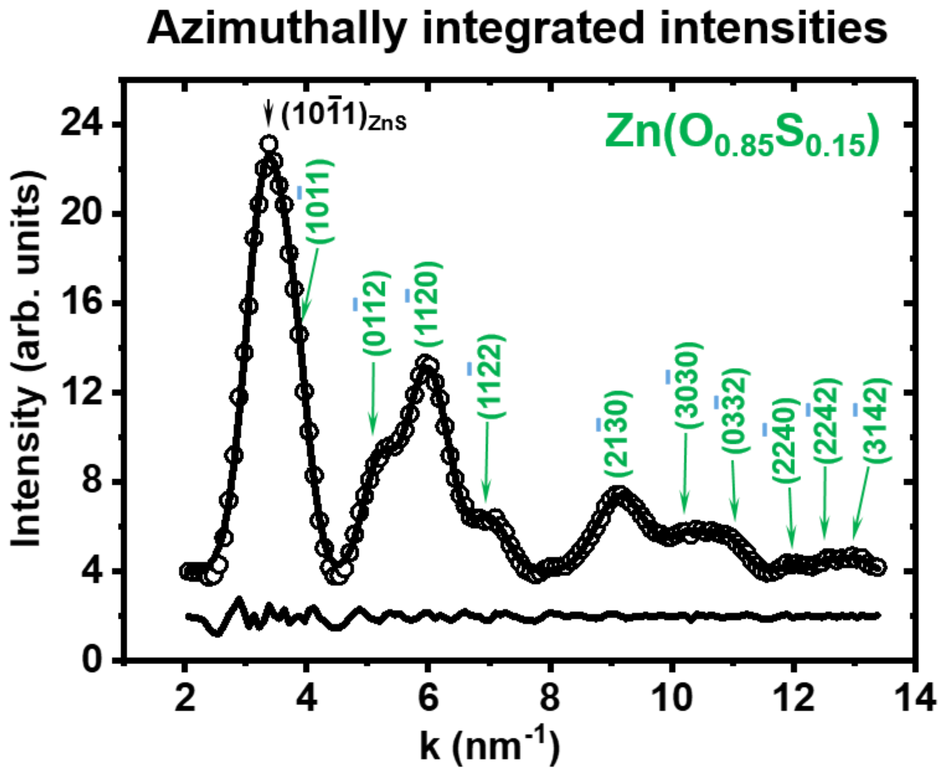
- As-grown Zn(O,S) layer $E_{Zn(O,S)}(x)$ = 2.89 eV ➔ hexagonal **$Zn(O_{0.28}S_{0.72})$** or **$Zn(O_{0.85}S_{0.15})$**
- Annealed Zn(O,S) layer $E_{Zn(O,S)}(x)$ = 2.85 eV ➔ hexagonal **$Zn(O_{0.30}S_{0.70})$** or **$Zn(O_{0.83}S_{0.17})$**
- Lattice parameters of the possible Zn(O,S) phases can be determined accordingly, which can be used to identify the present phase

[1] B.K. Meyer *et al.*, Appl. Phys. Lett. **85** (2004) 4929

Phase analyses of the Zn(O,S) buffers (as-grown)

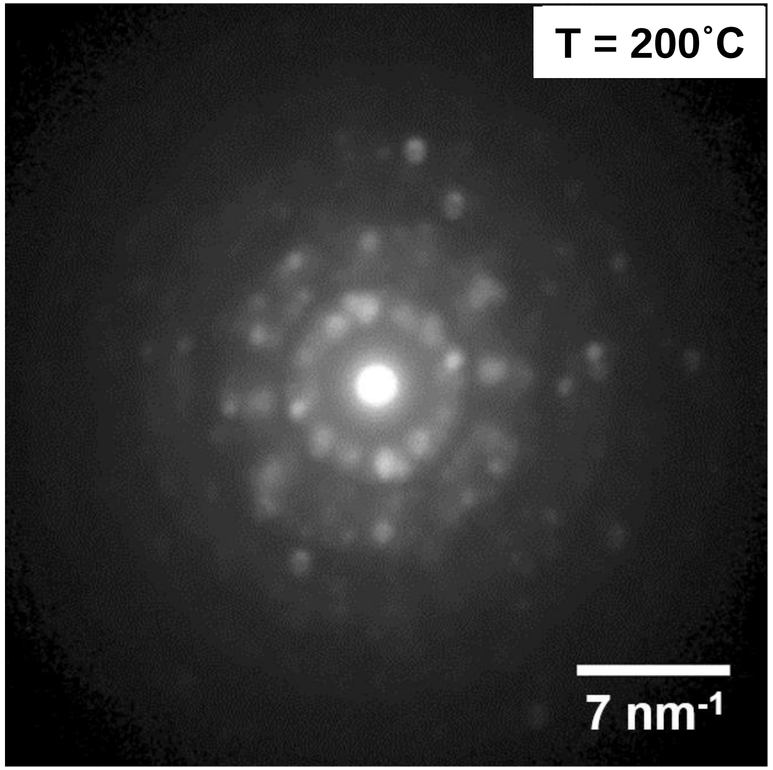
Karlsruhe Institute of Technology

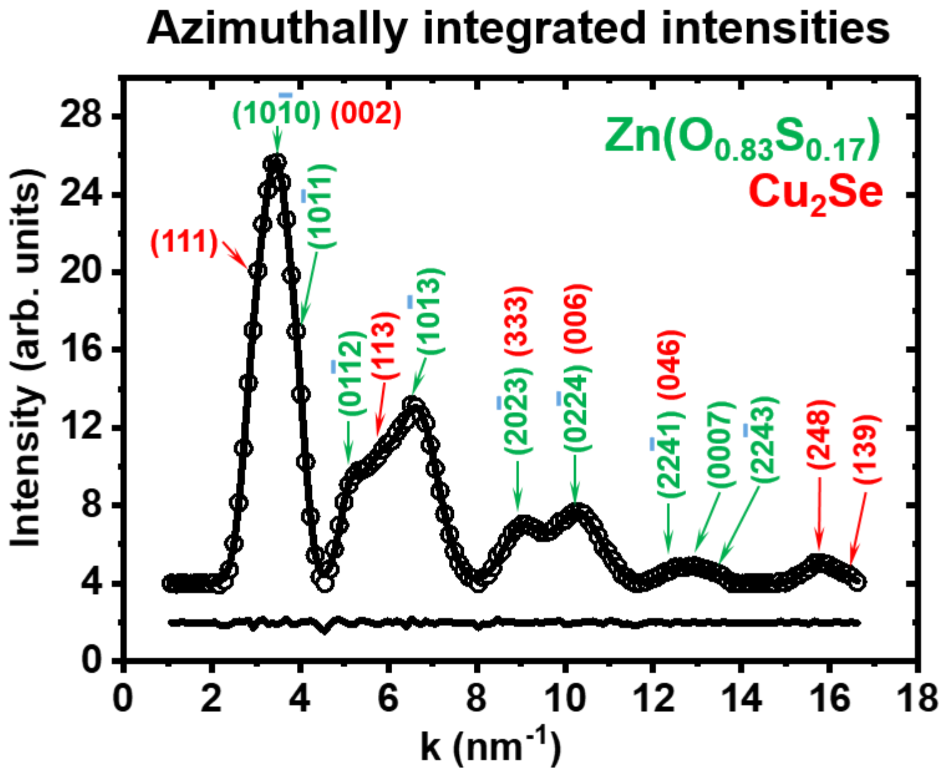




- $Zn(O_{0.85}S_{0.15})$ with wurtzite structure ($P6_3mc$, a = b = 3.3 Å, c = 5.3 Å) fits the NBD pattern better than $Zn(O_{0.28}S_{0.72})$, in agreement with the STEM/EDXS results
- ZnS with wurtzite structure ($P6_3mc$, a = b = 3.8 Å, c = 6.3 Å) may be also present in the buffer, whose bandgap (3.6 eV) cannot be detected by ARER (maximum 3.5 eV)

Phase analyses of the Zn(O,S) buffers (T = 200°C)

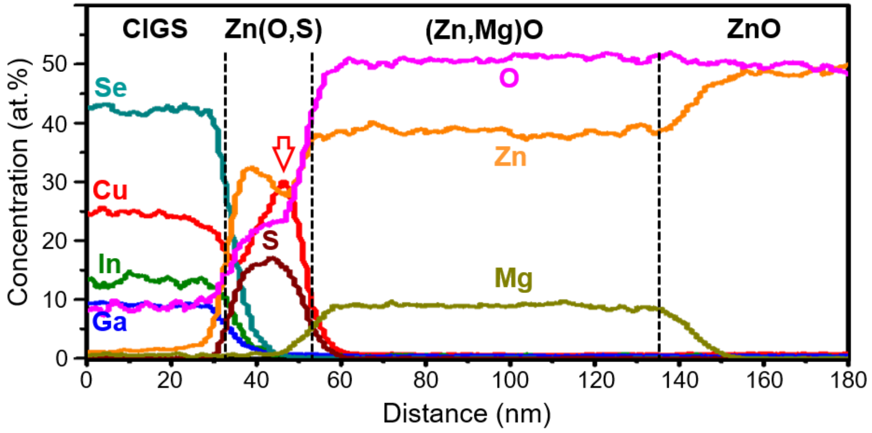


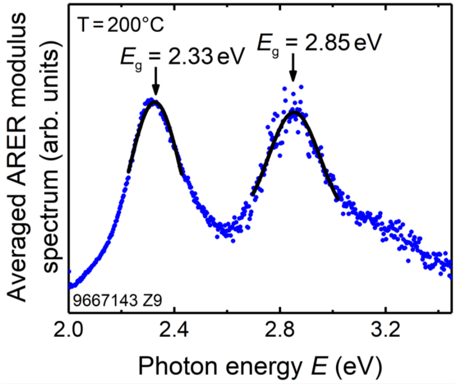


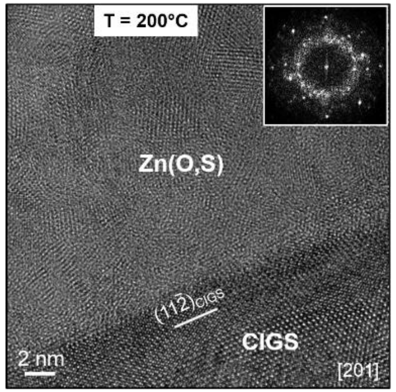
- $Zn(O_{0.83}S_{0.17})$ with wurtzite structure ($P6_3mc$, a = b = 3.3 Å, c = 5.4 Å) fits the NBD pattern better than $Zn(O_{0.30}S_{0.70})$
- Cubic Cu_2Se (Fm-3m, a = 5.7 Å) fits the NBD pattern of this region; hexagonal CuS ($P6_3mc$, a = b = 3.8 Å, c = 16.3 Å) exists in another region as shown by HRTEM imaging ➔ coexistence of Cu_2Se & CuS

Conclusions

- Annealing at 200˚C leads to Cu diffusion from CIGS into the solution-processed Zn(O,S) buffer layer, forming a secondary phase
- Cubic Cu_2Se and hexagonal CuS are the most likely Cu-containing secondary phases with a bandgap energy of ~2.3 eV
- Due to the limitations of ARER, HRTEM and NBD, other phases cannot be excluded
- Annealing at 200˚C does not significantly change the crystallinity (nanocrystalline) of the Zn(O,S) buffer layer, and slightly changes the stoichiometry of Zn(O,S)







Acknowledgement

Funding by the German Federal Ministry for Economic Affairs and Energy (BMWi) within the EFFCIS project under contract No. 0324076A (ZSW) and contract No. 0324076E (KIT) is greatfully acknowledged

Federal Ministry for Economic Affairs and Energy