In-situ XRD study on formation reactions of $\text{Cu}_2\text{ZnSnS}_4$ thin films

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Motivation

Kesterite ($\text{Cu}_2\text{ZnSnS}_4$) is a promising photovoltaic absorber material.

But:

Well performing solar cells with more than 3 % conversion efficiency are only obtained in long-term (> 5h) annealing processes [1,2].

The question is:

Is this due to a limited mobility of the different elements during film formation?

The aim of this study:

By varying the thickness of the precursor layers the influence of material transport can be modulated and evaluated.

With the experimental data we will estimate, whether long annealing times are necessary for the formation of kesterite thin films.

I) Precursor deposition

Variations:

- 1 cycle („1x1“)
- 2 cycles („2x1/2“)
- 4 cycles („4x1/4“)
- 8 cycles („8x1/8“)
- co-evaporation of all constituents („co-evap“)

Constant: Total film thickness (~ 2.2 μm)

Elemental ratios:

Cu/Zn ~ 1.8
 Cu/Sn ~ 2.3
 Zn/Sn ~ 1.3
 → Zn and Cu excess.

II) Energy Dispersive X-Ray Diffraction (EDXRD) during annealing

Annealing in elemental sulfur atmosphere.
 $p \sim 10^{-4}$ mbar
 $T_{\text{max}} \sim 500$ °C

In-situ detection of diffraction and fluorescence signals.

The Precursors

„1x1“

EDS-scan

- Layered precursor structure.
- ZnS with high SE-contrast.

„8x1/8“

- ZnS-contrast exhibits the layered structure.

Annealing of the precursors + in-situ EDXRD

„1x1“-measurement data:

Fitting of diffraction and fluorescence peaks for all precursor-types.

Reaction sequence:

- Starting phases: CuS, ZnS.
- Crystallization of SnS.
- Start of $\text{Cu}_2\text{ZnSnS}_4$ -formation.
- Transformation of CuS to Cu_{2-x}S .
- Consumption of copper- and tin-sulphides.

Qualitative result:

Decreasing thickness leads to lower temperature for kesterite formation.

After Annealing

„1x1“

- Large CuS-crystallites on film surface.
- Zn-excess remains in ZnS-precursor position.
- In the bottom part: no change of Zn/Sn-ratio in depth, increasing Cu-amount. → $\text{Cu}_2\text{ZnSnS}_4$ (+CuS).
- the limiting component SnS is completely transformed.

„8x1/8“

- Large CuS-crystallites on film surface.
- Zn-excess remains in ZnS-precursor position (small bright spots in SE-image).
- Elemental ratios roughly constant in the bottom layer.

Estimation of kinetic parameters from the EDXRD-data

Assumptions:

- 1-dimensional, diffusion controlled reaction of educt stacks.
- a three-stack reaction can be described by sequential two-stack reactions, with the slowest cation controlling the reaction.

Parameter determination:

The total thickness of formed kesterite is then given by [3]:

For T=const. (isothermal):

$$x(t, T) = c_{\text{cyc}} \cdot \sqrt{k_{\text{diff}} \cdot e^{-\frac{E_{\text{Adiff}}}{R \cdot T}} \cdot t}$$

For dT=β*dt (this study):

$$x(t, T') = \int_{T_0}^{T'} x(t, T) dT$$

c_{cyc} : no. of evap.cycles k_{diff} : preexp. factor (diffusion slowest cation)
 β : heating rate E_{Adiff} : activation energy (diff. slowest cation)
 R: gas constant

→ with T for $x(T)=2.2$ μm (reaction endpoint) for the different precursors, k_{diff} and E_{Adiff} can be calculated numerically.

Deriving the reaction endpoints from:

Case (A): Disappearance of SnS (vertical lines, extracted from upper graph))

Case (B): Significant drops in the derivate of the kesterite diffraction signal.

Parameter determination for different reaction endpoints:

Case	„8x1/8“ [°C]	„4x1/4“ [°C]	„2x1/2“ [°C]	„1x1“ [°C]	k_{diff} [cm ² /s]	E_{Adiff} [kJ/mol]
(A)	310	360	400	430	7×10^{-3}	105
(B)	320	380	410	430	1×10^{-2}	110

Example calculation:

At 500 °C a 2 μm thick layer is formed in about 70-90 seconds (according to case (A) and (B) respectively).
 → the formation of kesterite is fast !

Conclusion

An activation energy of about 105 kJ/mol and a preexponential factor of 7×10^{-3} cm²/s are estimated for diffusion controlled growth.

→ Fast formation of kesterite from sulfide-based precursors.

→ The long annealing times for well performing kesterite absorbers are not owing to a general kinetic limitation of kesterite formation.

References

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