Research Center for Photovoltaics

CZTSe系太陽電池の高効率化技術の開発

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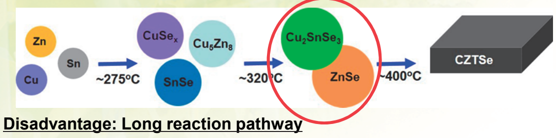
Introduction

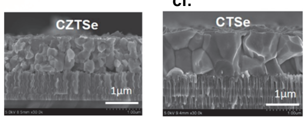
Conventional fabrication methods for CZTSe thin films

✓ Metal precursors (Pure metals and/or binary alloys)



Disadvantage: Long reaction pathway
(difficulty in the control of composition and secondary phases)

✓ Coevaporation

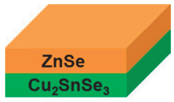


Disadvantage: Small grains of CZTSe thin films

Novel precursor proposed for CZTSe thin films

Cu_2SnSe_3 + ZnSe ⟷ $Cu_2ZnSnSe_4$

Hergert *et al.*, Thin Solid Films 515, 5953 (2007).
Wibowo *et al.*, Chem. Phys. 124, 1006 (2010).

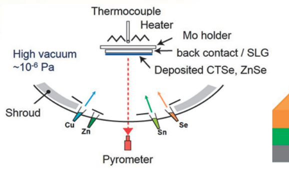


Advantage

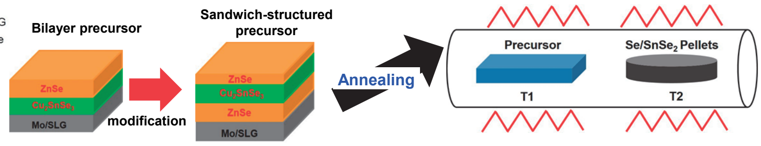
- More precise control of composition and secondary phases (short reaction path)
- Using CTSe with larger grains

Experimental

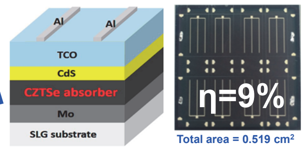
Growth method for precursors



Growth temperature: 340-370 °C
Thickness of precursors: ~ 1μm
Se vapor pressure >8×10^{-4} Pa

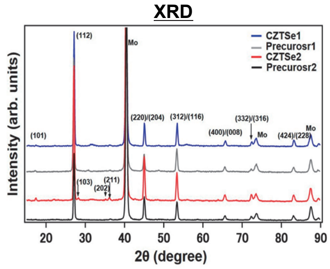


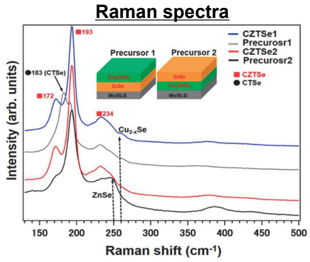
CZTSe solar cell structure



Results and Discussion

Effect of stacking order on CZTSe thin films properties





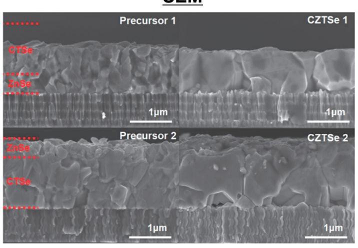
➡ CZTSe thin films were fabricated using the stacked precursors followed by annealing

Table 1. Elemental compositions of precursors and annealed CZTSe thin films

Sample	Cu (at%)	Zn (at%)	Sn (at%)	Se (at%)	Cu/(Zn+Sn)	Zn/Sn	
CZTSe1	26.3	8.3	12.2	53.2	1.28	0.68	➡ Cu-rich/Zn-poor
Precursor1	27.3	7.6	15.3	49.8	1.19	0.50	
CZTSe2	23.6	13.3	11.5	51.6	0.95	1.16	➡ Cu-poor/Zn-rich
Precursor2	23.9	14.1	12.2	49.8	0.91	1.16	

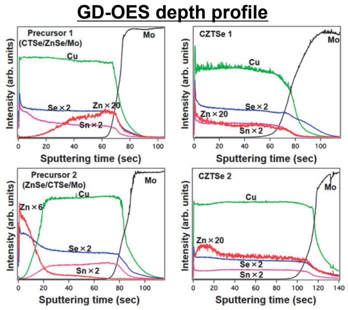
➡ The stacking order of precursors strongly affected the chemical composition of CZTSe thin films

SEM



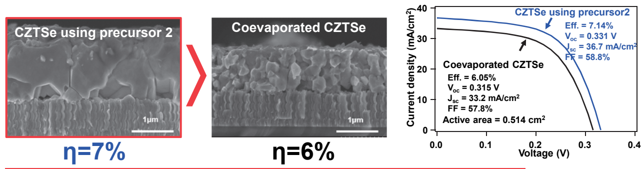
K.M. Kim *et al.*, Applied Physics Express, 8, 042301 (2015)
Selected as spotlights in Applied physics Express

GD-OES depth profile

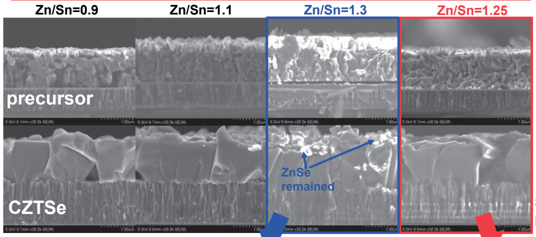


➡ Zn loss in precursor 1 (CTSe/ZnSe/Mo) occurred during the CTSe deposition.
Whereas Precursor 2 (ZnSe/CTSe/Mo) shows improved stability in composition.

CZTSe thin film with large grains was fabricated using ZnSe/CTSe precursor



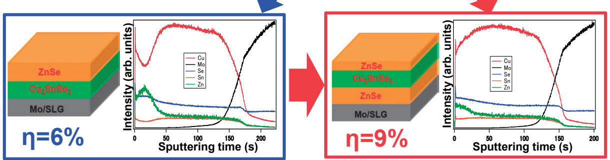
Control of Zn/Sn ratio by adjusting thickness of ZnSe layer



Poor performance of CZTSe using bilayer precursor (>Zn/Sn=1.1) due to excessive ZnSe formation on the surface region

To solve this problem

Sandwich-structured precursor proposed



Bilayer precursor　　Sandwich-structured precursor

The conversion efficiency significantly improved by Sandwich-structured precursor

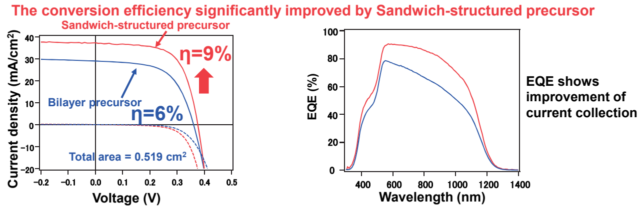


Table 2. Device parameter of CZTSe using bilayer and sandwich-structured precursors

Precursor structure	Zn/Sn ratio	Eff. (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)
ZnSe/CTSe	0.9	4.14	0.265	33.11	47.1
ZnSe/CTSe	1.1	6.77	0.35	34.26	56.4
ZnSe/CTSe	1.3	6.15	0.36	28.97	58.9
ZnSe/CTSe/ZnSe	1.25	8.96	0.375	37.3	63.9

Summary

✓ We successfully synthesized the CZTSe thin films with large and densely packed grains using Cu_2SnSe_3 (CTSe) and ZnSe precursors followed by annealing treatment.

✓ The chemical composition of CZTSe thin films was strongly dependent on the stacking order of precursors even under identical growth condition.

✓ Bilayer (ZnSe/CTSe/Mo) shows a relatively high conversion efficiency of over 7%, however, the efficiency was decreased with increasing the Zn content (Zn/Sn>1.1).

✓ The formation of ZnSe secondary phases on the surface of CZTSe thin films can be suppressed by sandwich-structured precursor (ZnSe/CTSe/ZnSe/Mo).

✓ The conversion efficiency was significantly improved from 6% to 9% by structural modification of precursor (bilayer precursor ➡ sandwich-structured precursor).