Research Center for Photovoltaics

Characterization of a 12.3% efficient $Cu_2Zn(Sn_{1-x}Ge_x)Se_4$ thin-film solar cell

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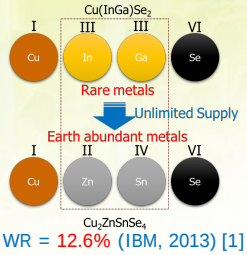
Introduction

CZTSe System

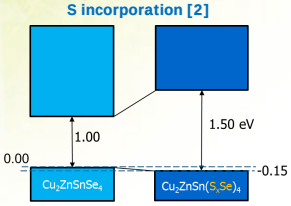
Next generation technology for CIGS

WR = 22.6% (ZSW, 2016)



WR = 12.6% (IBM, 2013) [1]

Motivation – Limited band-gap control of CZTSSe



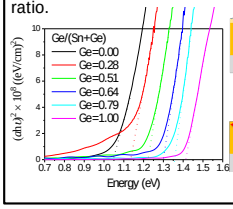
~1.0 < E_g(CZT(S_xSe_{1-x}))< ~1.5 eV

- The control of S/(S+Se) ratio is difficult due to the high volatility of the anionic components.
- Large V_{OC} deficit (E_g/q-V_{OC}) with S incorporation
  - CZTSe ≈ 0.577 V → CZTSSe ≈ 0.647 V, (at champion cells respectively)
  - Ex) CIGSe ≈ 0.5 V
- Low FF
  - Low V_{OC} and high ideality factor (A)

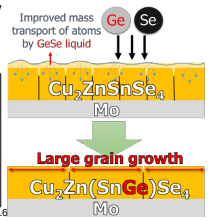
Ge incorporation effects in the CZTSe [3]

Band gap control

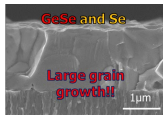
~1.0<E_g (CZTGSe)<~1.5 eV controlled by Ge/(Sn+Ge) ratio.



Large grain growth

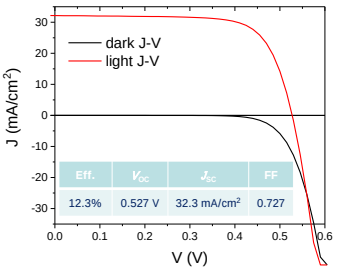


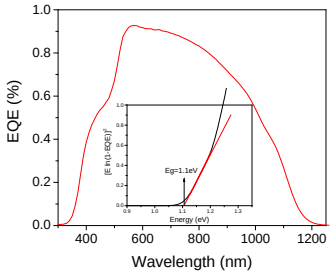
Demonstrated large grain growth method for $Cu_2Zn(SnGe)Se_4$



Results and Discussions

New efficiency of Ge incorporated kesterite solar cell





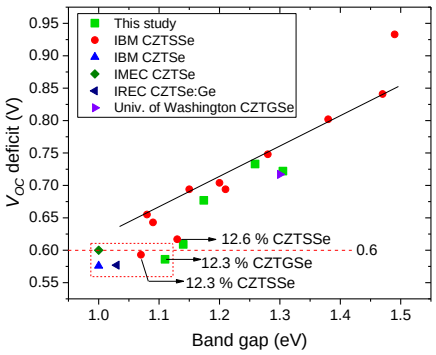
The highest efficiency of Ge incorporated kesterite solar cell greater than 12% [4]

Device parameters

Cell	Eff. (%)	V_{OC} (V)	J_{SC} (mA/cm²)	FF	R_s (Ω·cm²)	R_{sh} (Ω·cm²)	A	J_0 (A/cm²)	E_a (eV)	$E_a/q-V_{OC}$
CZTSSe IBM (2013)	12.60	0.513	35.2	0.698	0.72	621	1.45	7.0E-8	1.13	0.617
CZTGSe AIST (2015)	10.03	0.543	29.5	0.627	0.20	694	2.49	6.3E-6	1.19	0.647
CZTGSe AIST (2016)	12.32	0.527	32.2	0.727	0.36	1111	1.47	3.6E-8	1.11	0.583

Improved V_{OC} and FF with Ge incorporation
- V_{OC} deficit (= 0.583 V)
- Highly improved fill factor over 0.7

Reduced V_{OC} loss in the Ge incorporated kesterite solar cells

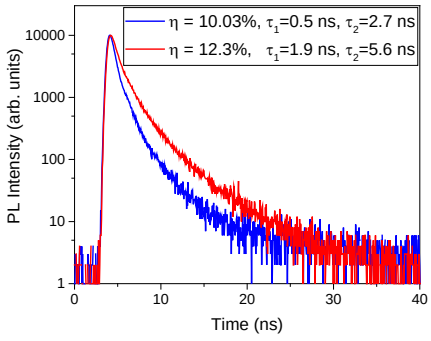


CZTGSe exhibits as in the follows.

- Small difference between lattice constant
  - CZTS: a = 5.435 Å, c = 10.843 Å
  - CZTSe: a = 5.693 Å, c = 11.333 Å
  - CZGSe: a = 5.606 Å, c = 11.042 Å
- Small interaction parameter
  - 5.6 mV/atom in $Cu_2ZnSn_{1-x}Ge_xSe_4$
  - 26 mV/atom in $Cu_2ZnSn(S_{1-x}Se_x)_4$

Reduced band tailing in comparison with CZTSSe.

Life time measurement of CZTGSe



- An extended τ_1 :
  - reduced recombination near the interface which is related to reduced A and J_0.
  - → Improved FF
- An extended τ_2 :
  - suppression of non-radiative recombinations in the bulk, which is related to the trapping in the deep levels.
  - → Improved V_{OC} deficit

Summary

We demonstrate new results of Ge incorporated kesterite thin-film solar cell.
- High efficiency 12.3%
- Small V_{OC} deficit (0.583 V)
  - reduced band tailing through control of the Ge/(Sn + Se) ratio
- Large improvement in FF (=0.727)
  - reduced carrier recombination at the absorber/buffer and/or SCR

References

[1]. W. Wang, M. T. Winkler, O. Gunawan, T. Gokmen, T. K. Todorov, Y. Zhu and D. B. Mitzi, Advanced Energy Materials, **4**, 1301465 (2014).

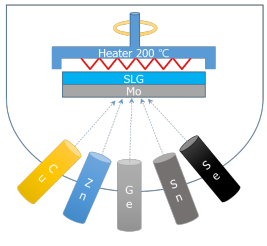
[2]. Q. Shu, J.-H. Yang, S. Chen, B. Huang, H. Xiang, X.-G. Gong and S.-H. Wei, Physical Review B, **87** 115208 (2013).

[3]. S. Kim, K. M. Kim, H. Tampo, H. Shibata, K. Matsubara and S. Niki, Solar Energy Materials and Solar Cells, **144** 488 (2016).

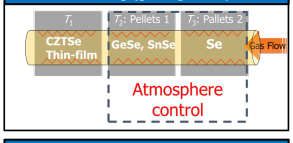
[4]. S. Kim, K. M. Kim, H. Tampo, H. Shibata and S. Niki, Applied Physics Express, **9** 102301 (2016).

Experimental Conditions

Co-evaporation



Annealing (grain growth)



CZTGSe solar cell structure