Research Center for Photovoltaics

Ge incorporated $Cu_2ZnSnSe_4$ thin-film solar cells

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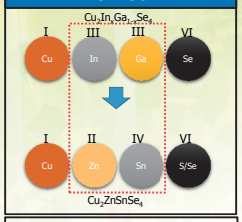
Introduction

CZTSe



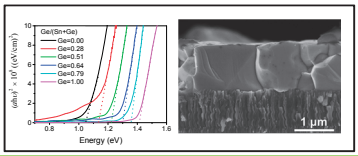
- In, Ga → Zn, Sn
- High absorption coefficient – α> 10^4 cm^{-1}
- Using the earth abundant materials
- Solar cell cost down

Problems of S incorporation

- 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 [1]
  - CZTSe ≈ 0.577 mV → CZTSSe ≈ 0.647, (at champion cells respectively)
  - Ex) CIGSe ≈ 0.5
- Low *FF* [2]
  - Low V_{OC} and high ideality factor (*A*)
  - Secondary phase problems

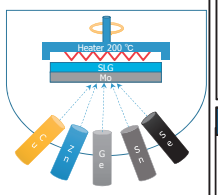
CZTGSe

- Tunable band-gap using cationic element
  → ~1.0<E_g(CZTGSe)<~1.5eV controlled by Ge/(Sn+Ge) ratio.
- Reduced V_{OC} deficit [3]
- Large grain growth caused by $GeSe_2$ liquid phase [4]



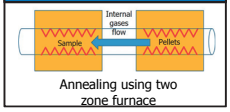
Experimental Conditions

Co-evaporation



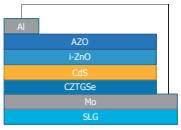
As grown CZTGSe deposited by co-evaporation

Annealing



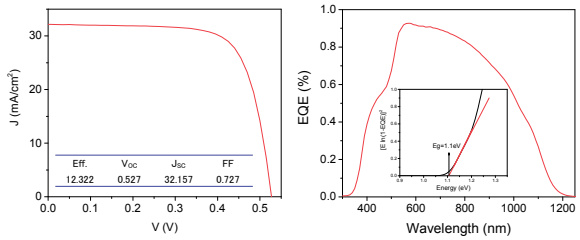
Annealing using two zone furnace

CZTGSe solar cell structure



Results and Discussions

New efficiency of Ge incorporated kesterite solar cell



- The highest efficiency of Ge incorporated kesterite solar cell greater than 12%

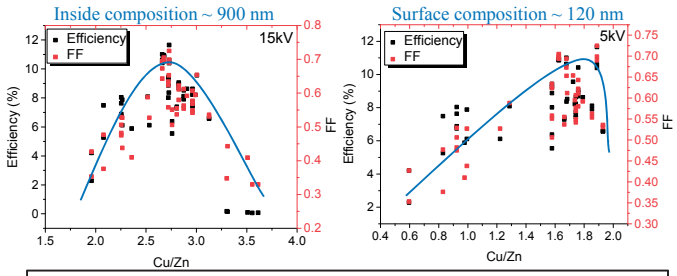
Device parameters

Cell	*Eff.* (%)	V_{OC} (V)	J_{SC} (mA/cm²)	*FF*	R_s (Ω·cm²)	R_{sh} (Ω·cm²)	*A*	J_o (*A*/cm²)	E_g (eV)	E_g/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

- Highly improved fill factor over 0.7
- Reduced device parameters – *A, J_o and V_{OC} deficit*

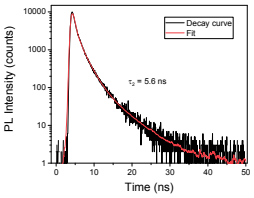
→ Improved junction quality and reduced carrier recombination in SCR

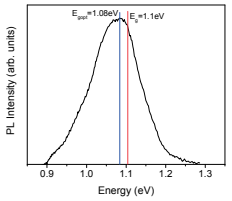
Cu/Zn ratio of CZTGSe thin films (EPMA)



- Efficiency shows similar tendency with *FF*.
- Optimized conditions are observed at Cu/Zn=2.7 (15kV) and 1.9 (5kV)
- Cu rich film but having slightly Cu poor surface is helpful to the improvement of *FF* and conversion efficiency.

Lifetime measurement by TRPL





Cell	*Eff.* (%)	Lifetime(ns)
CZTSSe IBM (2013)	12.60	6.7
CZTGSe AIST (2015)	10.03	2.5
CZTGSe AIST (2016)	12.32	5.6

- Improved carrier life time
- PL peak is closed to the band edge position (≈0.03) – it may be beneficial effect in reducing V_{OC} deficit

Summary

- We demonstrate new results of Ge incorporated kesterite thin-film solar cell.
  - – High efficiency greater than 12%
  - – Large improvement in FF over 0.7
  - – Improved junction quality and reduced carrier recombination in SCR
    - – *A*, J_0 and V_{OC}-deficit
  - – Increased carrier life time

Reference

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2. K. F. Tai, O. Gunawan, M. Kuwahara, S. Chen, S. G. Mhaisalkar, C. H. A. Huan and D. B. Mitzi, Advanced Energy Materials **6** (3), (2016).
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