Ge incorporated $Cu_2ZnSnSe_4$ thin-film solar cells

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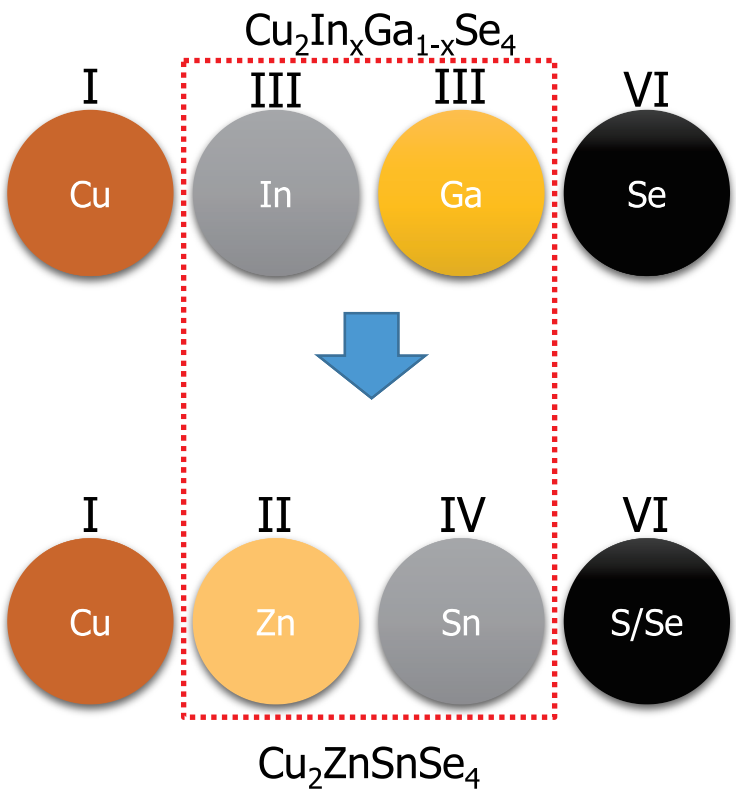
Introduction – Kesterite solar cells

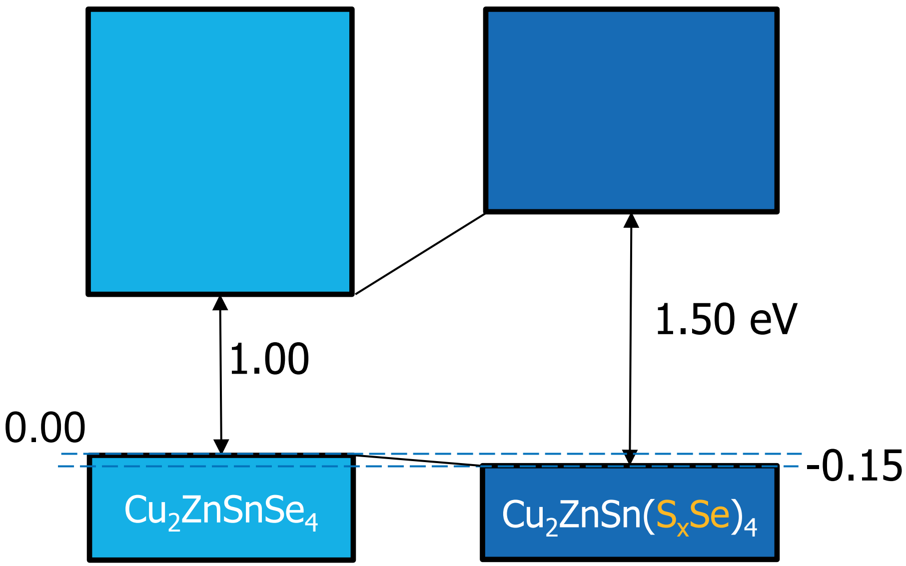
CZT(S)Se



- In, Ga → Zn, Sn
- High absorption coefficient
  - $\alpha > 10^4\ cm^{-1}$
- Using the earth abundant materials
- Production cost down

Introduction – Band gap tuning of kesterite thin films

Band gap tuning with S incorporation



$$\sim 1.0 < E_g(\mathrm{CZT}(S_xSe_{x-1})) < \sim 1.5\ \mathrm{eV}$$

Problems of S incorporation

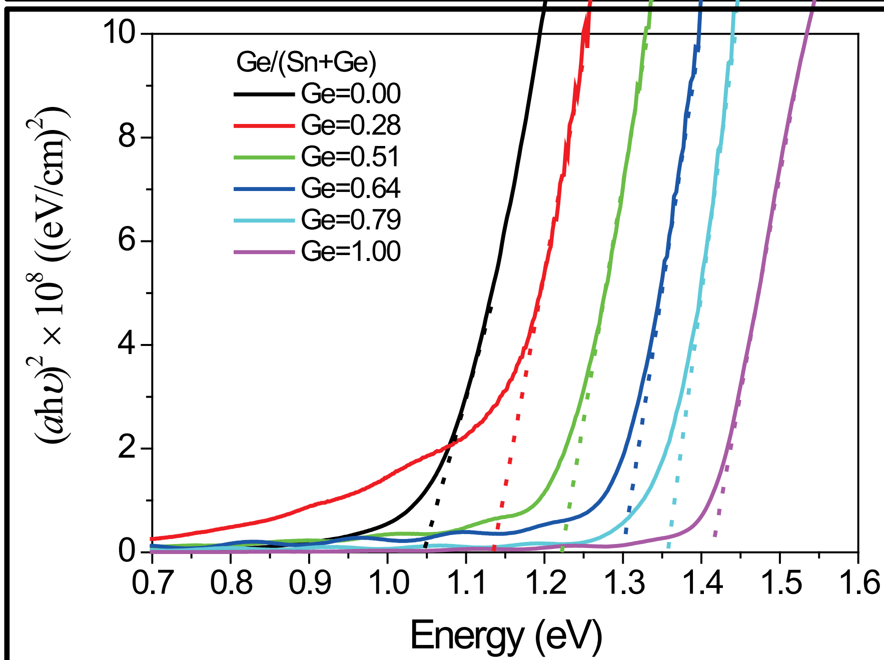
- The control of S/(S+Se) ratio is difficult due to the high volatility of the anionic components.
- Large V_{OC} deficit (E_g/q-V_{OC}) with S incorporation [1]
  - CZTSe ≈ 0.577 mV → CZTSSe ≈ 0.647, (at champion cells respectively)
  - Ex) CIGSe ≈ 0.5
- Low *FF* [2]
  - Low V_{OC} and high ideality factor (*A*)
  - Secondary phase problems

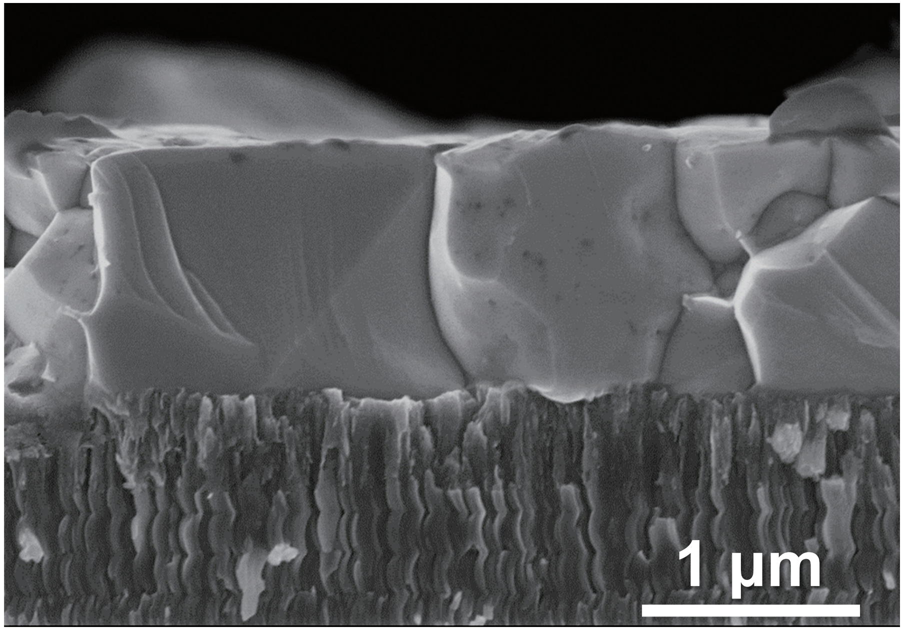
1. A. Polizzotti *et al*., Energy & Environmental Science **6** (11), 3171-3182 (2013).
2. K. F. Tai *et al*., Advanced Energy Materials **6** (3), (2016)

Ge incorporated CZTSe (CZTGSe)

CZTGSe

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





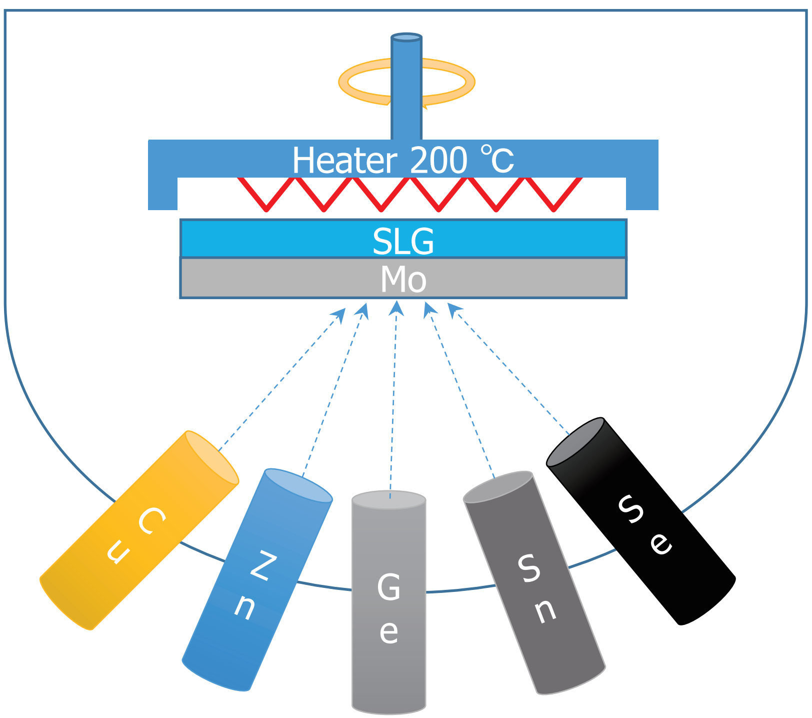
I-V Results of Ge incorporated Cells

Cell	*Eff.* (%)	V_{OC} (V)	J_{SC} (mA/cm²)	*FF* (%)	E_g (eV)	$E_g/q-V_{OC}$
CZTGSSe Perdue Univ. (2013) [1]	9.40	0.460	31.9	63.8	1.19	0.730
CZTGSe AIST (2015) [2]	10.03	0.543	29.5	62.7	1.19	0.647
CZTSe IREC(2015) [3]	10.60	0.473	34.3	65.1	1.03	0.550
CZTGSe Univ. of Washington (2016) [4]	11.00	0.583	33.6	55.9	1.30	0.717

1. C. J. Hages *et al.*, Progress in Photovoltaics: Research and Applications **23** (3), 376-384 (2013).
2. S. Kim *et al.*, Solar Energy Materials and Solar Cells **144**, 488-492 (2016).
3. S. Giraldo *et al.*, Advanced Energy Materials **5** (21), (2015).
4. A. D. Collord and H. W. Hillhouse, Chemistry of Materials **28** (7), 2067-2073 (2016).

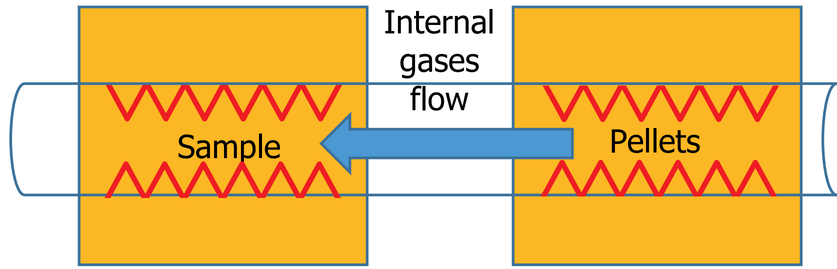
Experimental Procedure

Co-evaporation



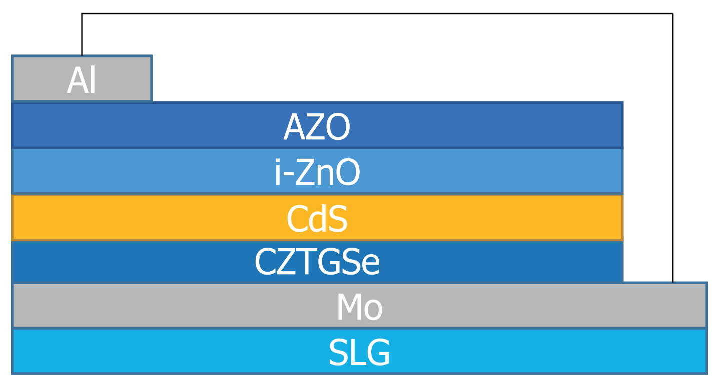
As grown CZTGSe deposited by co-evaporation method.
Composition Control

Annealing

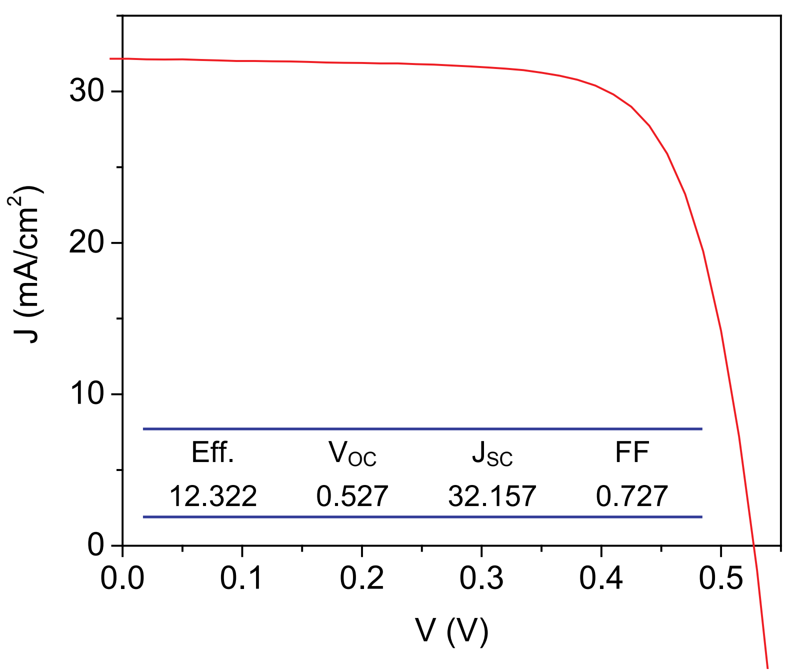


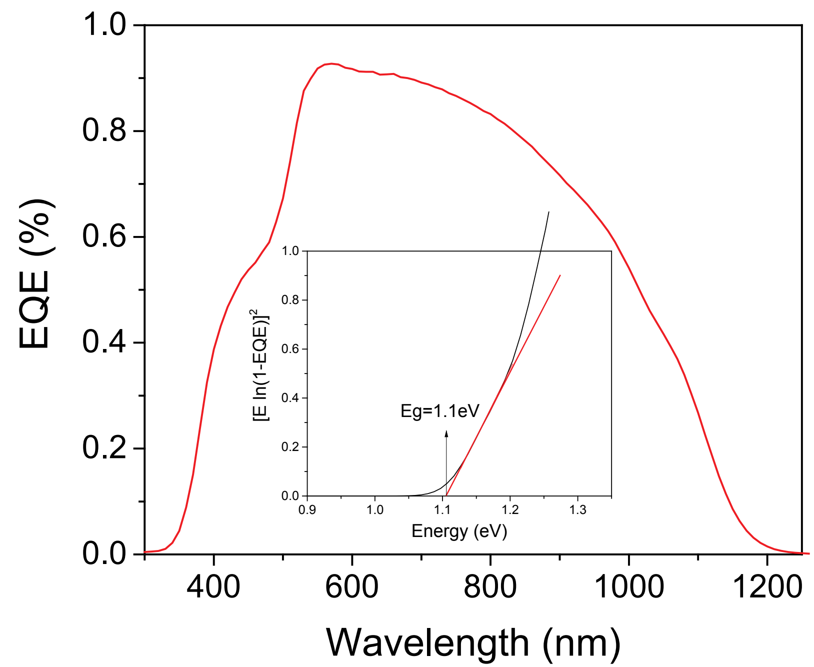
Annealing using two zone furnace
Grain Growth

CZTGSe solar cell structure



New efficiency of Ge incorporated kesterite solar cell





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

Device parameters

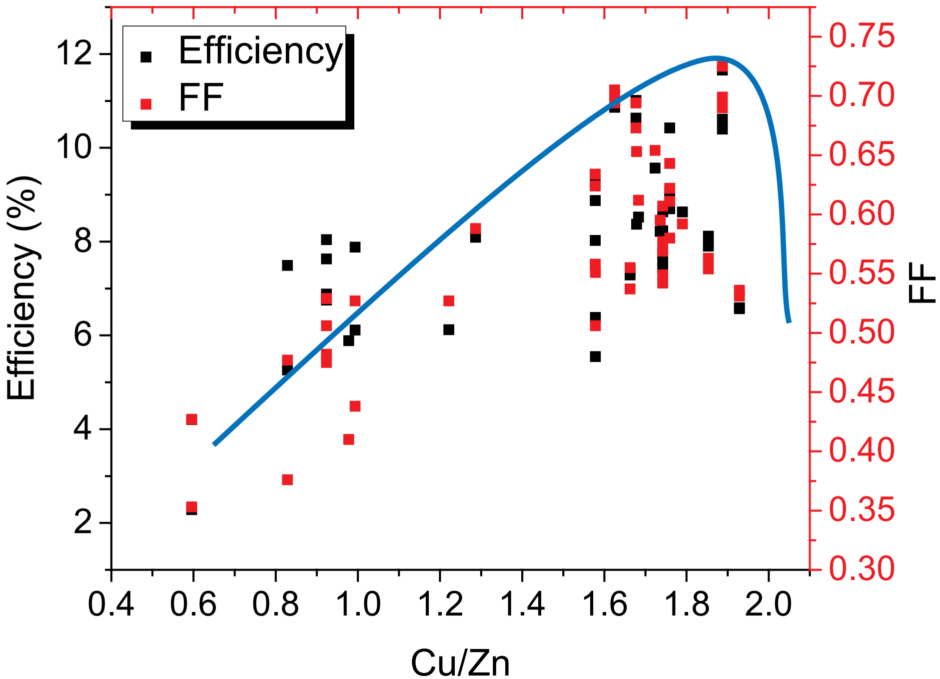
Cell	*Eff.* (%)	V_{OC} (V)	J_{SC} (mA/cm²)	*FF*	R_s (Ω·cm²)	R_{sh} (Ω·cm²)	*A*	J_0 (A/cm²)	E_g (eV)	$E_g/q-V_{OC}$
CZTSSe IBM (2013)	12.60	0.513	35.2	0.698	0.72	621	1.45	7.0E-8	1.13	0.617
CZTGSe AIST (2015)	10.03	0.543	29.5	0.627	0.20	694	2.49	6.3E-6	1.19	0.647
CZTGSe AIST (2016)	12.32	0.527	32.2	0.727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

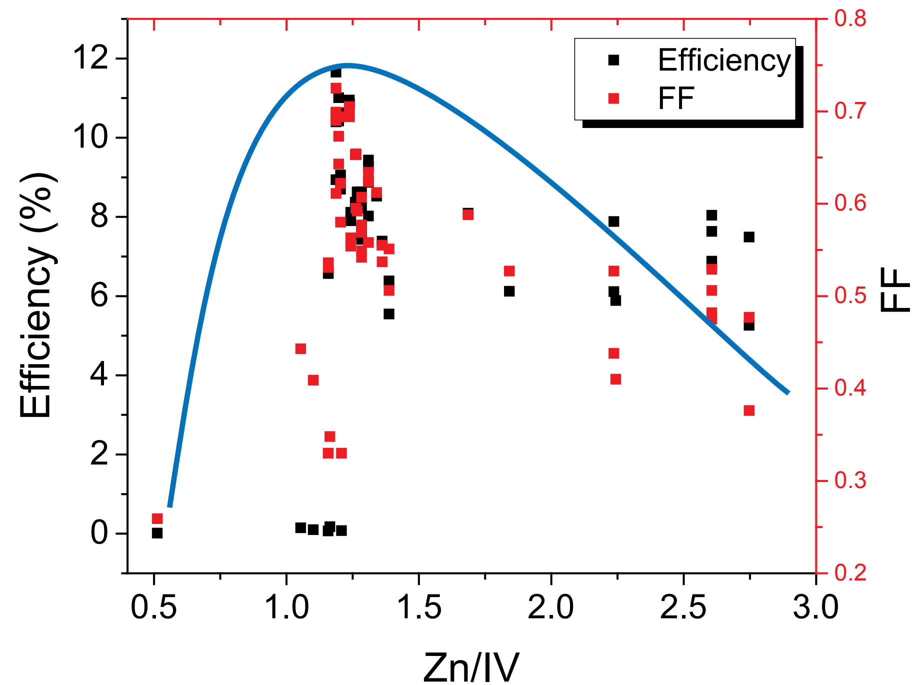
- Highly improved fill factor over 0.7
- Reduced device parameters – *A*, J_o *and* V_{OC} *deficit*

→ Improved junction quality and reduced carrier recombination in SCR

Atomic ratio of CZTGSe thin films (EPMA)

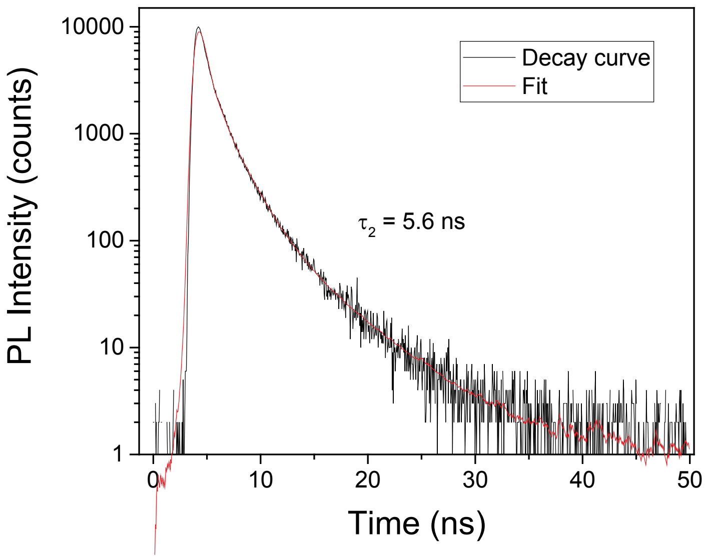
Surface composition ~ 120 nm



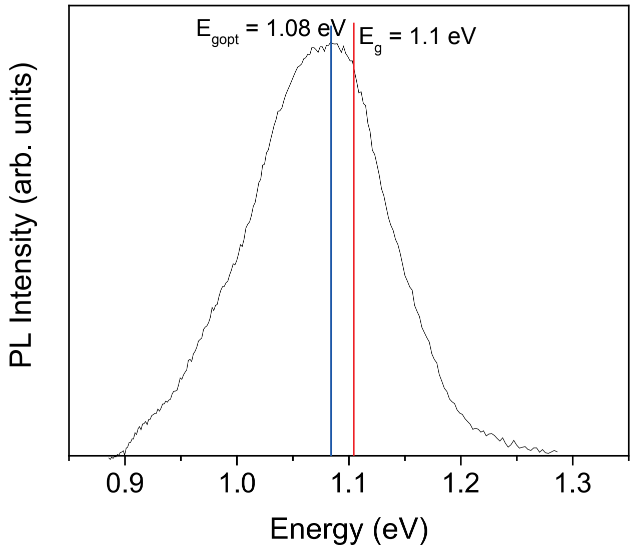


- Efficiency shows similar tendency with *FF*.
- Optimized surface conditions are observed at Cu/Zn=1.9 and Zn/IV=1.2.

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

Thank you for your attention!