# Development of Ge incorporated CZTSe thin-film solar cells

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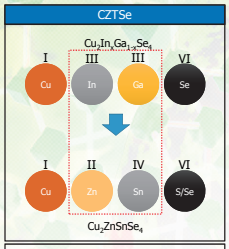
## Introduction




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

### Motivation – Limited band-gap control of CZTSSe

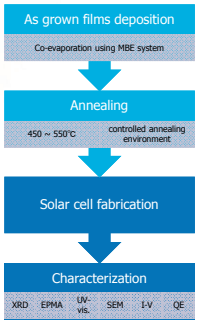
- $E_g$(CZTSe) = ~1.0 eV → ~1.0 < $E_g$(CZT($S_xSe_{x-1}$)) < ~1.5 eV
- The control of S/(S+Se) ratio is difficult due to the high volatility of the anionic components.
- High S/(S+Se) ratios exhibit a deeper defect level and increased defect density.*

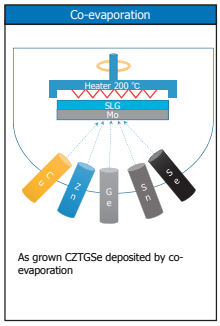
*Duan et al., Advanced Functional Materials 23 (11) 2013.

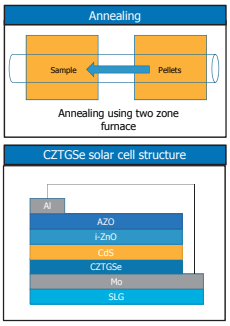
### Objective - Ge incorporated CZTSe thin films

- Tunable band-gap using cationic element
  - ➢~1.0 < $E_g$(CZTGSe) < ~1.5 eV controlled by Ge/(Sn+Ge) ratio.
- Smaller effective mass of carrier than CZTSSe
  - ➢Beneficial effect to the device conductivity
- High miscibility of Ge into the CZTSe.
  - ➢Simpler and easier composition control than anionic elements

## Experimental Conditions

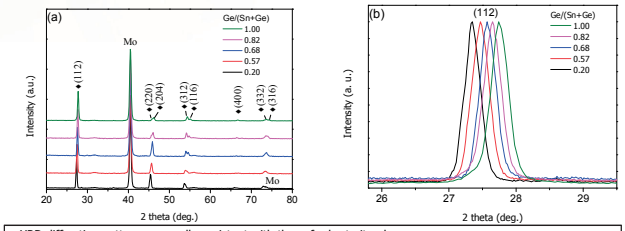


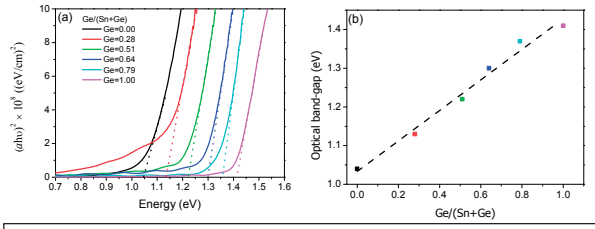

## Results and Discussions

### XRD results with various amount of Ge incorporation



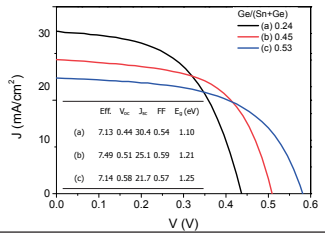

- XRD diffraction patterns are well consistent with those for kesterite phase.
- Kesterite peaks shifted to higher 2 theta angle with increasing Ge incorporation.
- Unit cell of CZTGSe is reduced with Ge incorporation.
  - Lattice constant: [CZTSe a = 5.693 Å, c = 11.333 Å], [CZGSe a = 5.606 Å, c = 11.042 Å]
- XRD reveals Ge atoms well incorporated into the CZTSe.

### Band-gap of the CZTGSe thin films



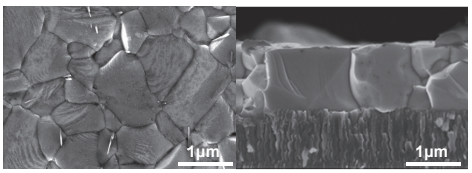

- The band-gap of CZTGSe was controlled in the full range of 0 < Ge/(Sn+Ge) < ~1.
- The band-gap of CZTGSe is increasing almost linearly with increasing the Ge/(Sn+Ge) ratio.
  → The band-gap bowing of CZTGSe thin films is small.

### Ge incorporation vs. $V_{oc}$




- Typical dependence of $V_{OC}$ on the $E_g$ of CZTGSe thin-film solar cells
- $V_{OC}$ of CZTGSe is increased with increasing amount of incorporated Ge, while $J_{SC}$ was decreased.

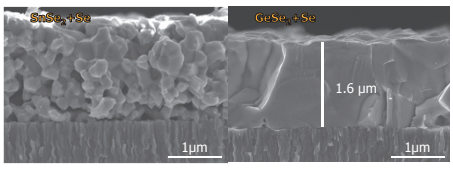
### Morphology of CZTGSe thin film




- Large grain comparable with its film thickness
- Flat surface
- Dense and void-free morphology

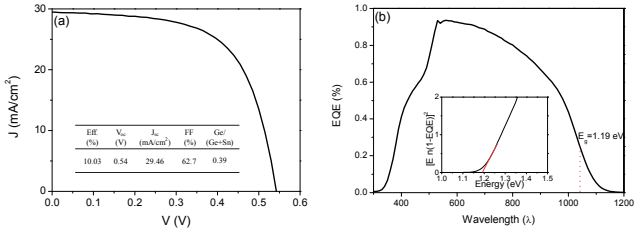
→ Beneficial effect to the $V_{oc}$ of a CZTGSe

### The annealing environment effects




- CZTSe thin films annealed under [$GeSe_2$+Se] and [$SnSe_2$+Se] environments.
- Annealing environment containing $GeSe_2$ led to improved morphological properties.

### I-V and QE Results of CZTGSe




**High efficiency CZTGSe thin-film solar cell with efficiency greater than 10%**

### I-V Results

| Cell | Eff. (%) | $V_{OC}$ (V) | $J_{SC}$ (mA/cm$^2$) | FF (%) | $E_g$ (eV) | $E_g/q-V_{OC}$ |
|---|---|---|---|---|---|---|
| CZTSSe – IBM (2013) | 12.6 | 0.513 | 35.2 | 69.8 | 1.13 | 0.617 |
| CZTSSe – IBM (2013) | 11.1 | 0.460 | 34.5 | 69.8 | 1.13 | 0.670 |
| CZTGSSe – Perdue Univ. (2013) | 9.4 | 0.460 | 31.9 | 63.8 | 1.19 | 0.730 |
| CZTGSe – AIST (2015) | 10.03 | 0.543 | 29.5 | 62.7 | 1.19 | 0.647 |

- Improved $V_{oc}$ of 0.543 V with $E_g$ = 1.19 eV
- $V_{oc}$ deficit is similar with CZTSSe thin film solar cell of 11.1%.

## Summary

- CZTGSe thin films were prepared and their material and device properties were examined.
- The band-gap of CZTGSe was controlled in the full range of 0<Ge/(Sn+Ge)<1.
- The annealing environment containing $GeSe_2$ led to improved morphological properties.
- We demonstrated CZTGSe thin-film solar cell with efficiency greater than 10% and a high $V_{oc}$ value of 0.54 V.