Research Center for Photovoltaics

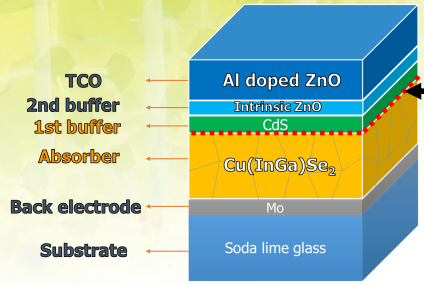
Surface sulfurization study on the CIGSe thin-film solar cell

Shinho Kim[1], Sekizen Takaesu[1], Hitoshi Tampo[1], Hajime Shibata[1], and Shigeru Niki[1, 2]
National Institute of Advanced Industrial Science and Technology (AIST)
[1]Research Center for Photovoltaics, [2]Department of Energy and Environment

Introduction

Motivation: Improving V_{OC} loss in CIGSe

$Cu(InGa)Se_2$ (CIGSe) Thin-film solar cell

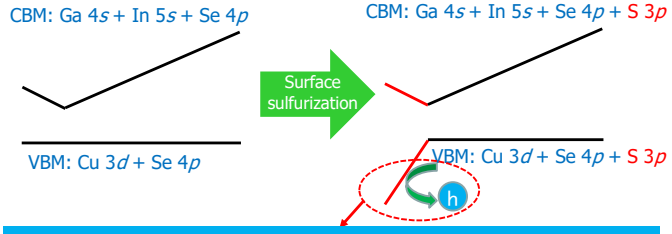


Research Target
High quality CdS/CIGS interface for small V_{OC} loss

V_{OC} deficit = $E_g/q - V_{OC}$
Crystalline Si = 0.36 V
CIGS = 0.4 ~ 0.5 V

Advantage of Surface Sulfurization on the CIGSe

Schematics of energy band of CIGSe



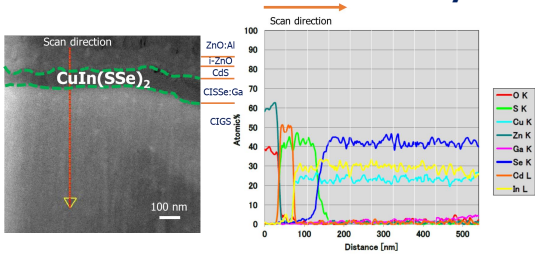
The downward valence band behaves as a hole-blocking barrier
→ **Reduced interface recombination → Reduced V_{OC} deficit**

Results and Discussion

Composition of CIGSe before and after sulfurization (measured by EPMA)

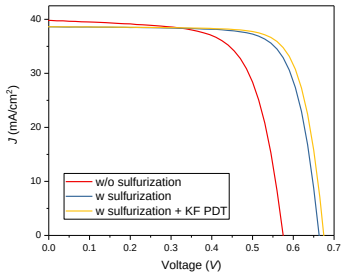
Analyzed depth from sample surface (acceleration voltage)	before sulfurization			after sulfurization		
	Cu/ (Ga+In)	Ga/ (Ga+In)	S/ (S+Se)	Cu/ (Ga+In)	Ga/ (Ga+In)	S/ (S+Se)
1.5 μm (20 kV)	0.92	0.15	0.00	0.89	0.13	0.16
0.1 μm (5 kV)	0.76	0.02	0.00	0.66	0.01	0.89

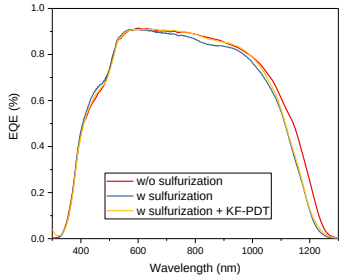
TEM-EDS analysis



- ✓ Graded S contents cause front graded bandgap.
- ✓ Ga intensity was very low in the near interface region.
- ✓ After sulfurization Ga doped CISSe (CISSe:Ga) was formed on the CIGSe layer.

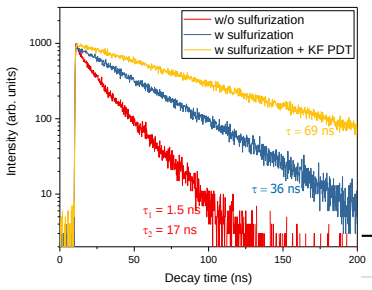
J-V and EQE analysis



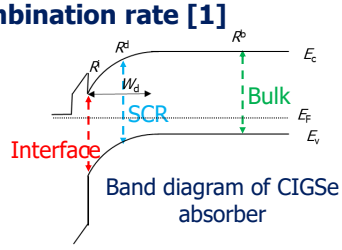


Sample	Eff. (%)	V_{OC} (V)	J_{SC} (mA/cm²)	FF	R_{SH} (kΩ·cm²)	R_S (Ω·cm²)	A	J_0 (mA/cm²)	E_g (eV)	$E_g/q - V_{OC}$ (V)
without Sulfur	15.5	0.58	39.8	0.68	0.33	0.32	1.92	3.6.E-04	1.07	0.49
with Sulfur	19.4	0.66	38.6	0.76	3.13	0.37	1.48	1.0.E-06	1.09	0.43
with S +KF PDT	20.1	0.68	38.6	0.77	3.03	0.37	1.40	3.1.E-07	1.09	0.41

Carrier lifetime measurement (TRPL) and calculated recombination rate [1]



$$I(t) = I_1(0)\exp(-\frac{t}{\tau_1}) + I_2(0)\exp(-\frac{t}{\tau_2}),$$



Band diagram of CIGSe absorber

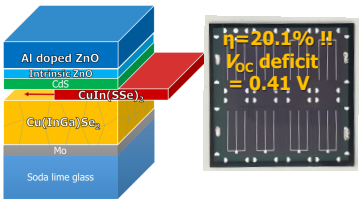
Recombination rate at $V = V_{OC}$ and T = 25 °C

Sample	Interface, R^I ($cm^{-2}\cdot s^{-1}$)	SCR, R^d ($cm^{-2}\cdot s^{-1}$)	Bulk, R^b ($cm^{-2}\cdot s^{-1}$)
w/o sulfurization	1.7 X 10^{17}	6.7 X 10^{17}	2.5 X 10^{18}
w sulfurization	3.6 X 10^{15}	2.6 X 10^{16}	1.5 X 10^{17}
with sulfurization +KF-PDT	3.2 X 10^{15}	2.1 X 10^{16}	9.9 X 10^{16}

The KF-PDT device shows improved carrier lifetime in bulk.

Summary

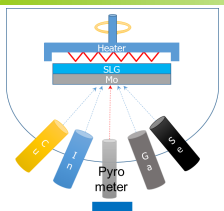
- ✓ Demonstrated surface sulfurization effect on the CIGSe
  - ✓ Reduction of recombination at buffer/CIGSe interface
  - ✓ Reduction of V_{OC} loss
- ✓ Demonstrated reduction of recombination in bulk by KF-PDT on the surface sulfurized CIGSe
  - ✓ Achieved high efficiency of 20.1%
  - ✓ Achieved small V_{OC} deficit of 0.41 V



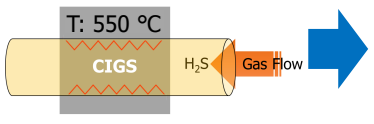
References

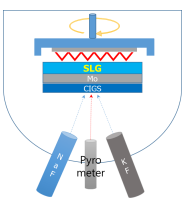
[1] J. V. Li, S. Grover, M. A. Contreras, K. Ramanathan, D. Kuciauskas, and R. Noufi, Sol. Energy Mater. Sol. Cells, **124** (2014) 143.

Experimental Conditions



- ✓ Single graded CIGSe using MBE
- ✓ Ga was not incorporated at 3rd stage.
- ✓ Surface sulfurization in the annealing furnace
- ✓ Alkali-PDT using MBE chamber





Annealing pressure: 5 ~ 8 X 10^4 Pa