Surface sulfurization study on the CIGSe thin-film solar cell

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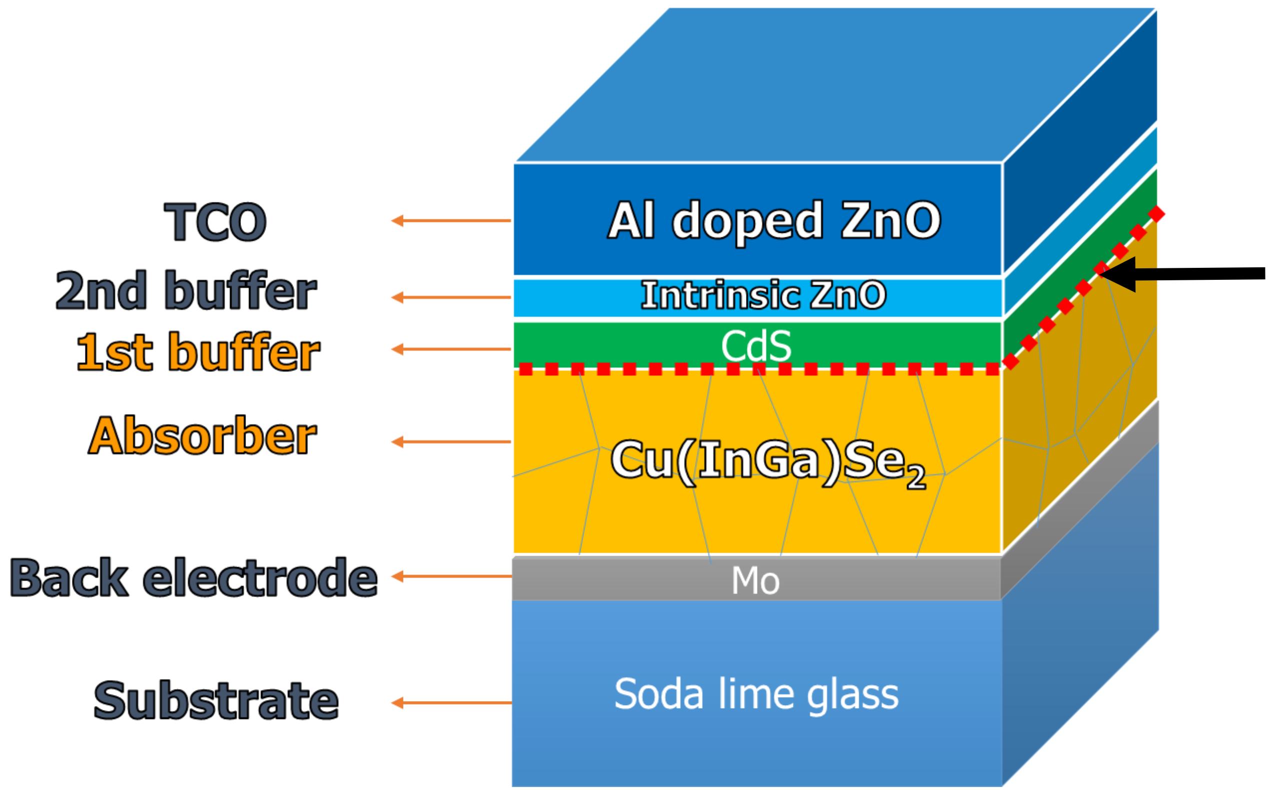
Structure of CIGSe/Research Target

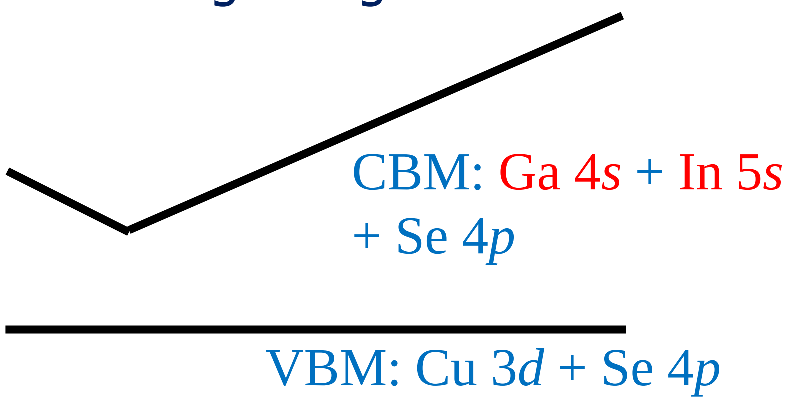


Research Target

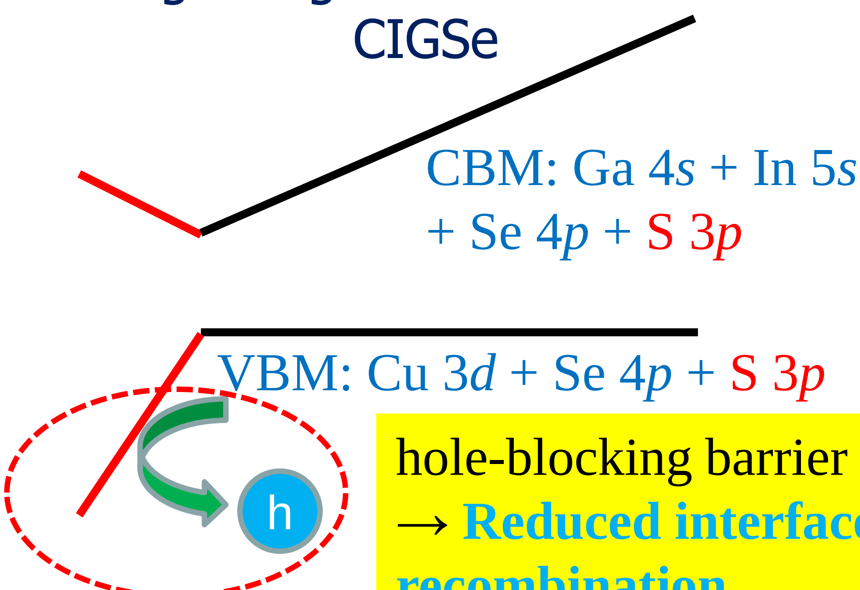
High quality CdS/CIGS interface for small V_{OC} loss

Surface sulfurization

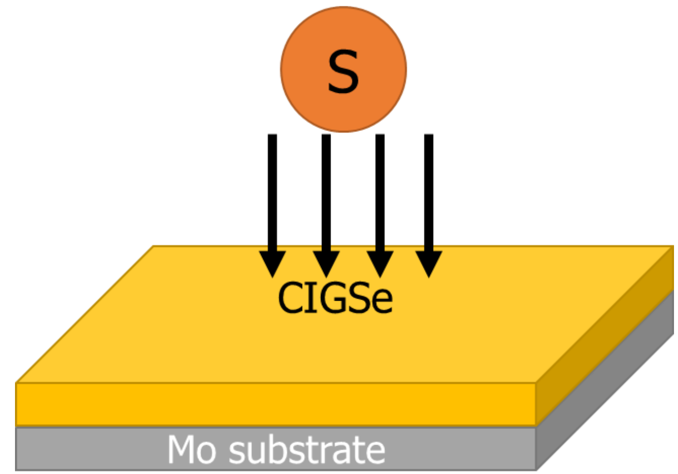
Band grading of CIGSe

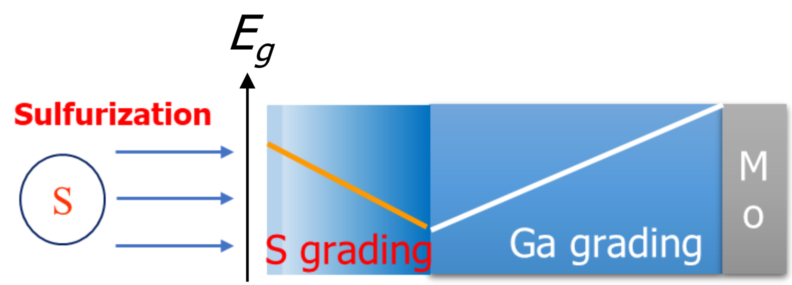


Band grading of surface sulfurized CIGSe



hole-blocking barrier
→ **Reduced interface recombination**

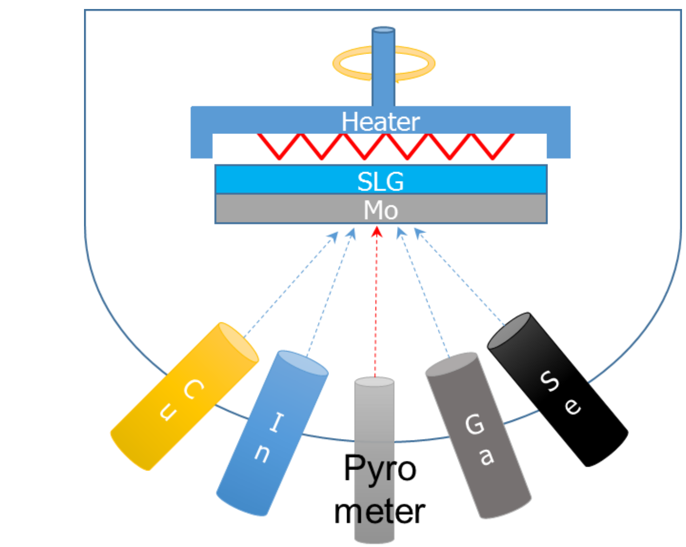


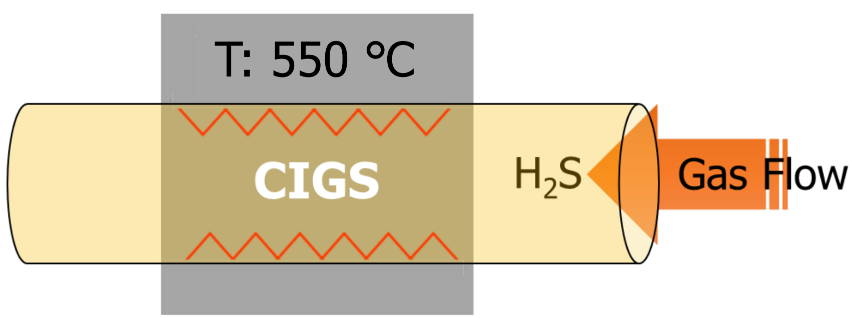


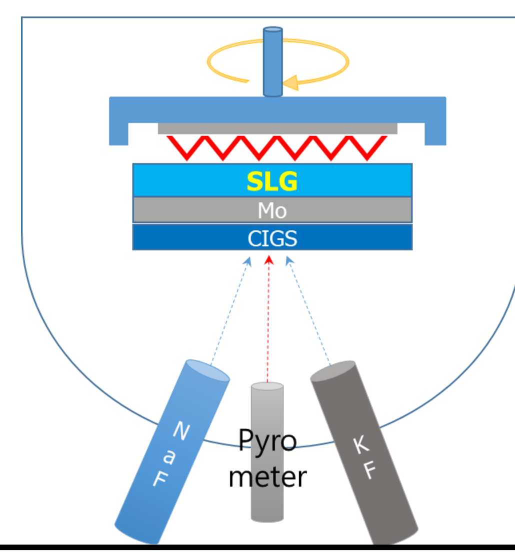
- Forming single graded bandgap CIGSe
- Forming front bandgap grading by incorporation of S

Experimental Method

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



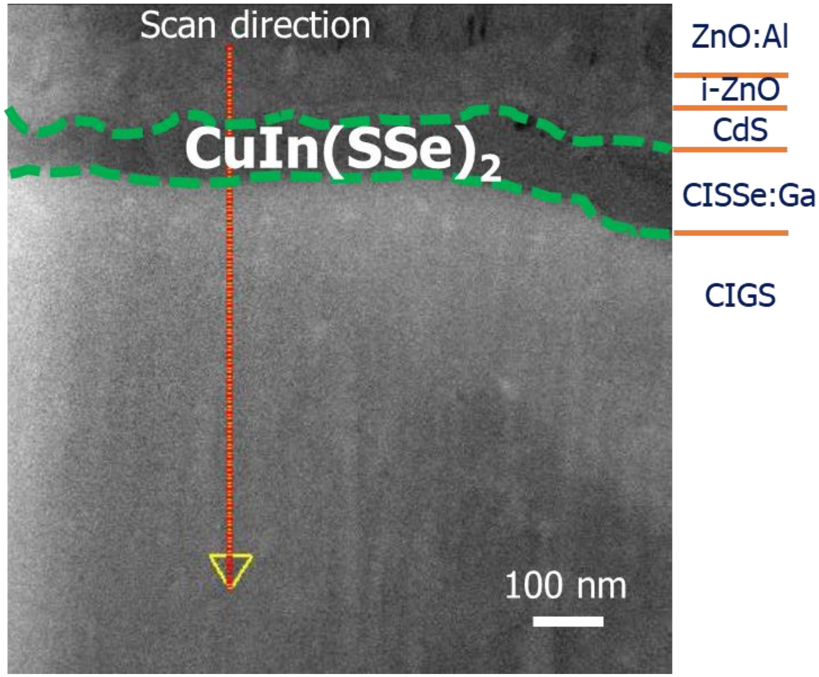


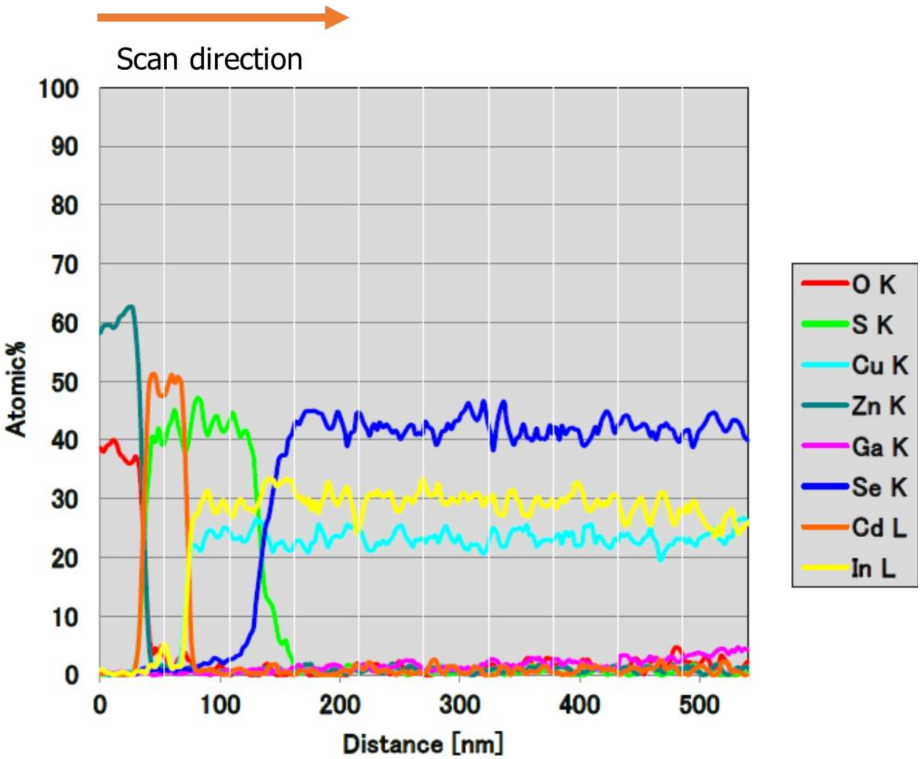


Annealing pressure: 5 ~ 8 X 10^4 Pa

Depth profile of surface sulfurized CIGSe

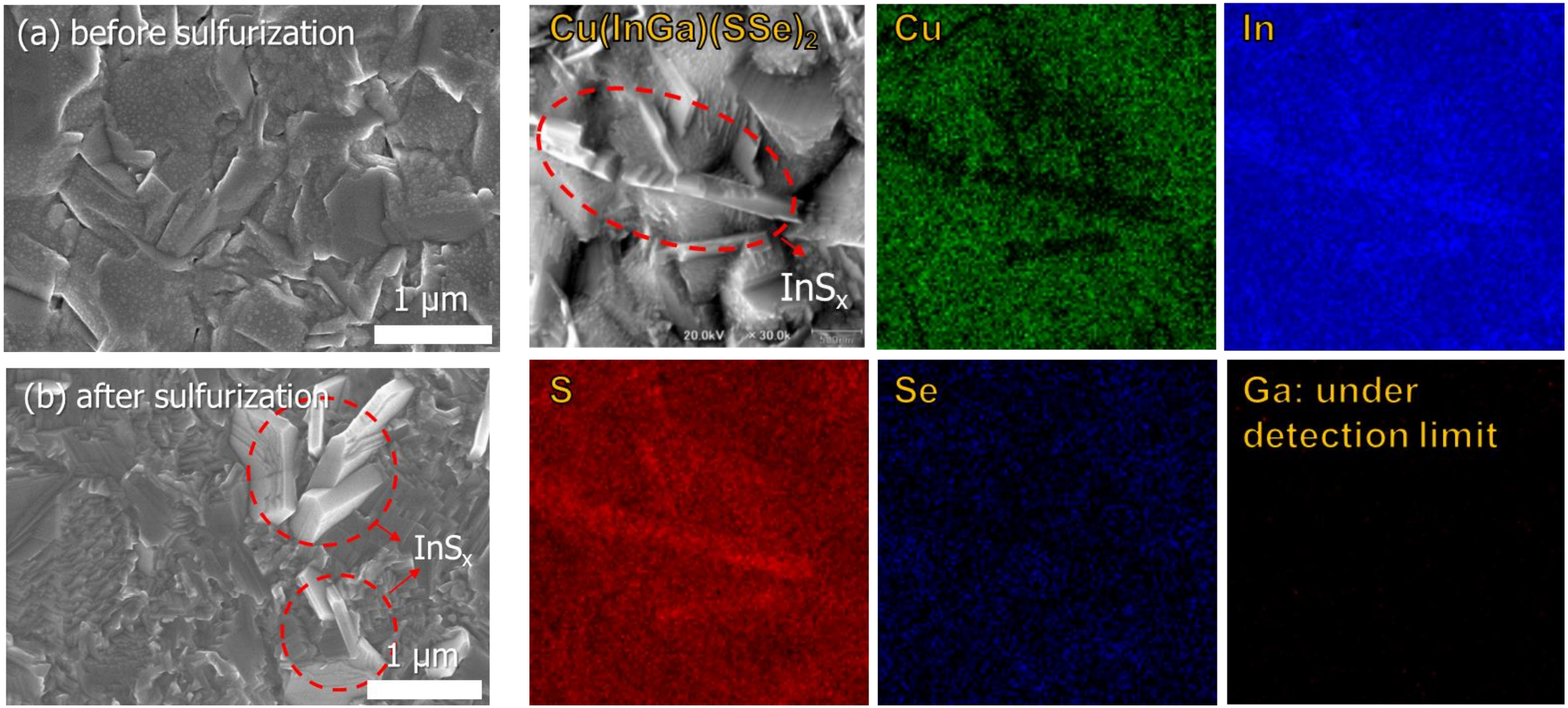
TEM-EDS analysis





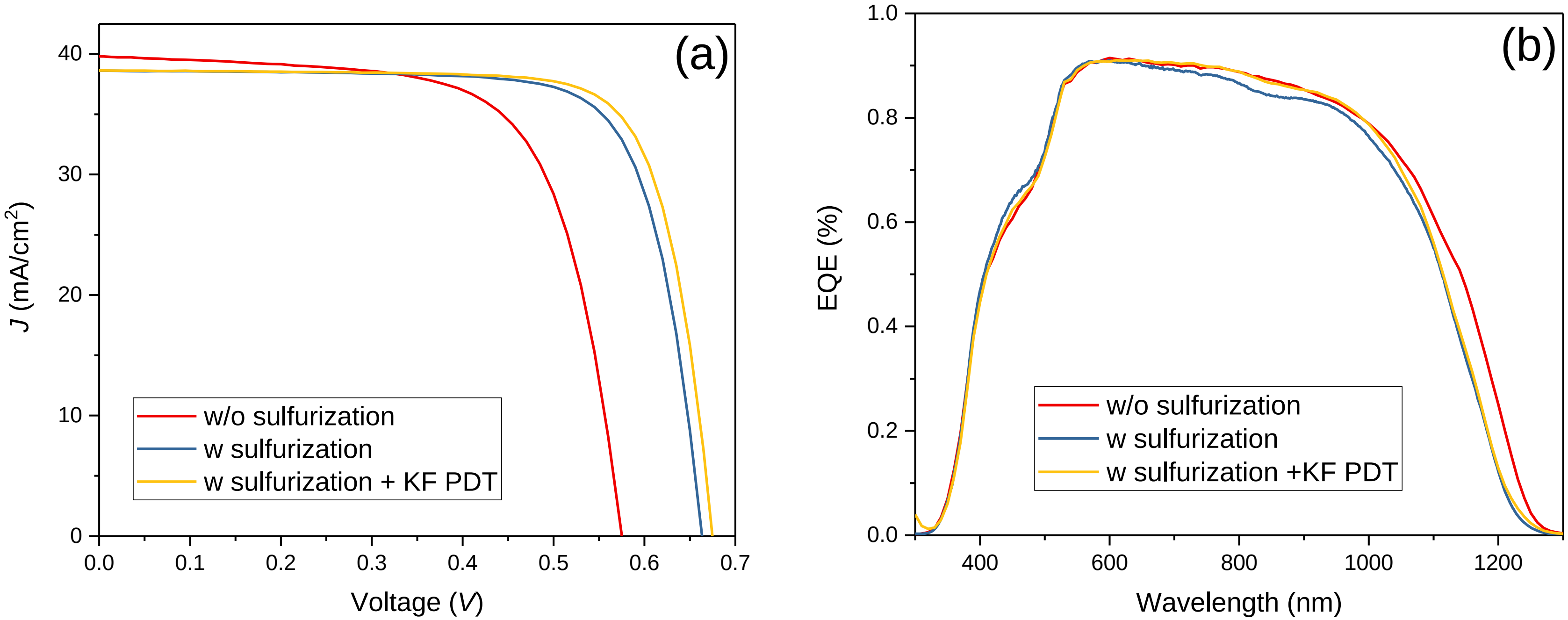
- ✓ Graded S contents cause front-graded bandgap.
- ✓ Ga intensity was very low in the near interface region.
- ✓ After sulfurization Ga doped CISSe (CISSe:Ga) was formed on the CIGSe layer.

Surface morphology (SEM) and surface elemental mapping images (measured by AES)



- ✓ After sulfurization Ga was not detected at the surface sulfurized CIGSe.
- ✓ Very thin CISSe was formed.
- ✓ InS$_x$ secondary phase was observed. → no harmful effects on the devices

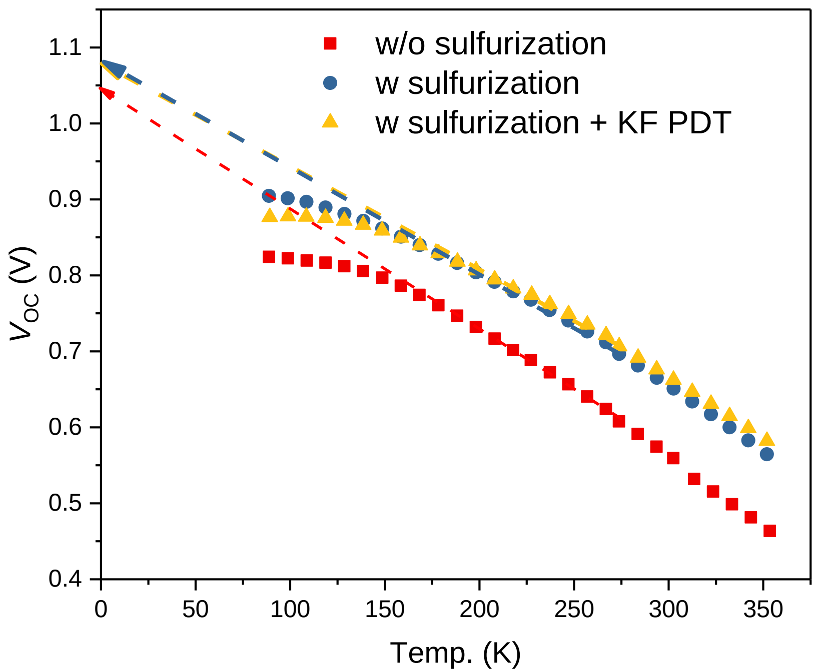
J-*V* and EQE analysis



Sample	Eff. (%)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	R_{SH} (kΩ·cm^2)	R_S (Ω·cm^2)	A	J_0 (mA/cm^2)	E_g (eV)	E_g/q-V_{OC} (V)
w/o S	15.5	0.58	39.8	0.68	0.33	0.32	1.92	3.6.E-04	1.07	0.49
w S	19.4	0.66	38.6	0.76	3.13	0.37	1.48	1.0.E-06	1.09	0.43
w 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

Reduced interface recombination

Activation energy (E_a) measured by temp. dependence of *J*-*V* analysis



- $E_g > E_a$
  $\rightarrow$ Large interface recombination
- The CIGSe with surface sulfurized exhibits almost same E_a.

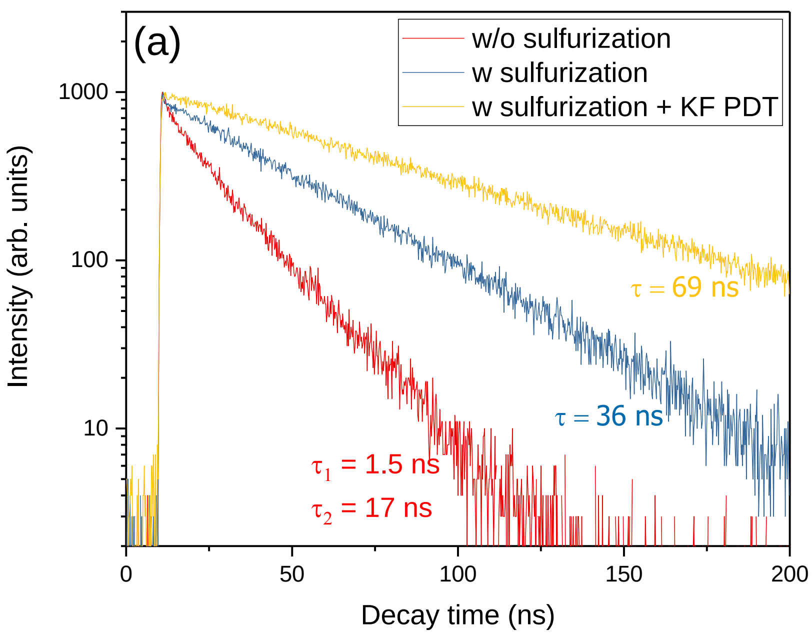
Sample	E_g (eV)	E_a (eV)
w/o S	1.07	1.04
w S	1.09	1.08
w S +KF PDT	1.09	1.08

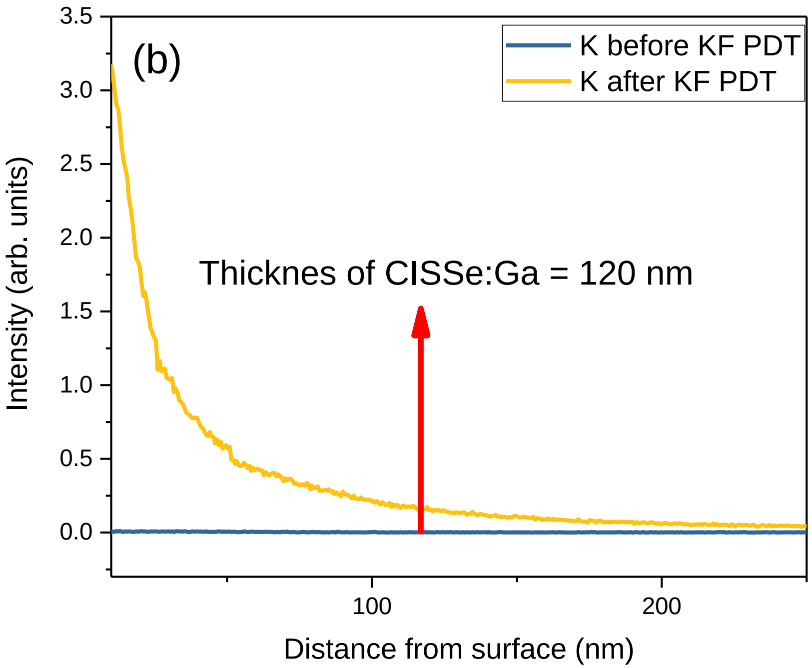
✓ Newly formed CISSe:Ga layer was effective in reducing interface recombination → Front graded bandgap and hole blocking layer

✓ What is the role of KF-PDT?

The role of KF-PDT

Carrier lifetime measurement (TRPL) and depth profile of CIGSe with KF PDT (GD-OES)



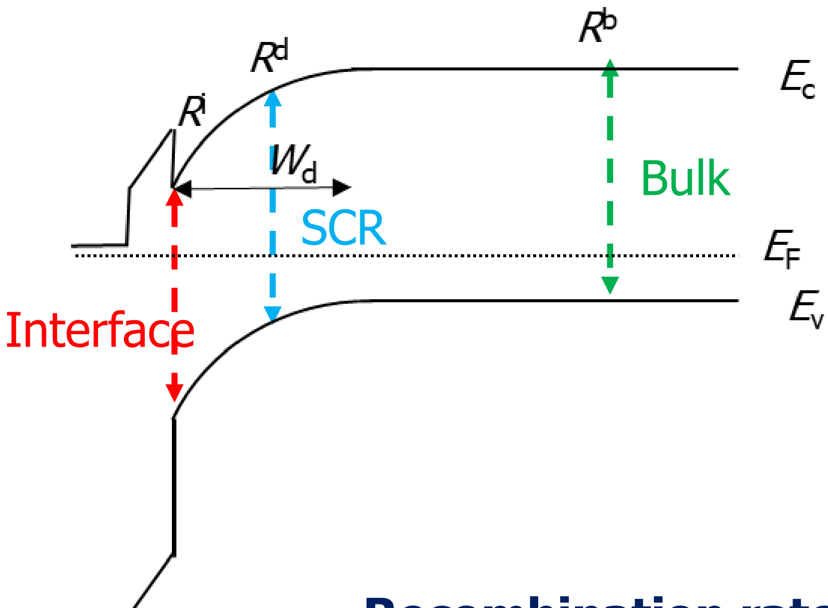


$$I(t) = I_1(0)\exp(-\frac{t}{\tau_1}) + I_2(0)\exp(-\frac{t}{\tau_2}),$$

- The KF-PDT device shows improved carrier lifetime in bulk.
- K penetrated bulk region of CIGSe.
- Defect passivation, grain boundaries passivation, etc.

Reduction of recombination

Band diagram of CIGSe absorber



$$V_{OC} = \frac{2kT}{q} \ln\left[\frac{1}{2}\frac{R_0^d}{R_o^i + R_0^b}\left(\sqrt{4GW\frac{R_0^i + R_0^b}{(R_0^d)^2} + 1} - 1\right)\right]$$

$$E_a = \frac{R_0^i q\varphi_{b0} + R_o^b E_g}{R_o^i + R_0^b}$$

$R^i = R_0^i e^{qV/kT}$, $R^d = R_0^d e^{qV/2kT}$ and $R^b = R_0^b e^{qV/kT}$

J. V. Li, S. Grover, M. A. Contreras, K. Ramanathan, D. Kuciauskas and R. Noufi: Solar Energy Materials and Solar Cells, **124** (2014) 143.

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	1.7×10^{17}	6.7×10^{17}	2.5×10^{18}
w sulfurization	3.6×10^{15}	2.6×10^{16}	1.5×10^{17}
with sulfurization +KF-PDT	3.2×10^{15}	2.1×10^{16}	9.9×10^{16}

Summary

- ✓ Demonstrated surface sulfurization effect on the CIGSe.
  - ✓ Newly formed CISSe:Ga layer was effective in 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