High Performance CZTSSe Solar Cell by Using Cadmium Free Non-toxic Zn(O,S) Buffer Layer

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In this work, we have demonstrated the non-toxic Zn(O,S) as an alternative buffer layer for CdS by chemical bath deposition (CBD) and atomic layer deposition (ALD) . One is chemical bath deposition (CBD) that is simple and well prepared. The other is atomic layer deposition (ALD) that can deposit uniformity for atomic level as well as the conformal coverage over large-scale areas. The Zn (O, S) buffer layer band gap (3.5eV) is wider than CdS (2.4eV) which can achieve higher short-circuit current (Jsc) density due to the enhanced transmission of the wavelength region between 350nm and 550 nm.

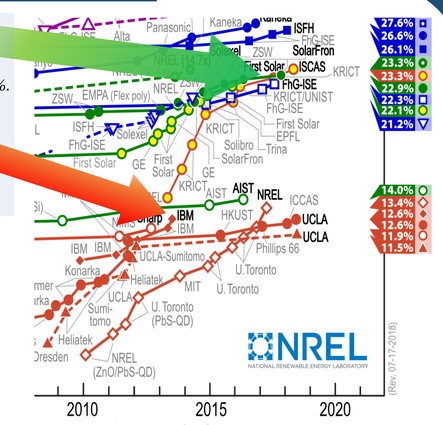
Finally, we obtained 5.4% efficiency of CZTSSe solar cell with open circuit voltage (V_{oc}) of 440 mV, short-circuit current density (J_{sc}) of 25 mA/cm^2, and fill factor (FF) of 50.2% by chemical bath deposition (CBD) ZnOS. Subsequently, we got 9.77%(~ 10.75% in the cell effective area) efficiency with open circuit voltage (V_{oc}) of 460mV, short-circuit current density (J_{sc}) of 36.07 mA/cm^2, and fill factor (FF) of 58.06 % by atomic layer deposition (ALD) ZnOS, which is the highest reported efficiency of CZTSSe with a Cd-free buffer layer. Apart from this, we successfully established the number of precursor cycles using the ALD process to control the O/S ratio and thickness. It helps us adjust the appropriate conduction band offset (CBO) to avoiding an unfavorable band.

Motivation

CIGS solar cell (22.9%) by Solar Frontier
- *Cu, In, Ga, Se (Chalcopyrites)*
- *Commercialized thin film solar cell*
- *promising PV material which demonstrated PCE over 22%.*

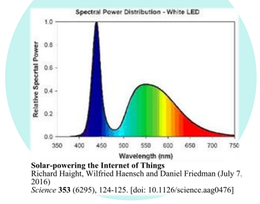
CZTSSe solar cell (12.6%) by IBM
- ***Cu, Zn, Sn, S or Se***
- ***Similar structure to CIGS (Kesterites)***
- ***Unlike CIGS, CZTS is composed of only abundant and non-toxic elements***

Advantages
- ✓ **Earth abundant and non-toxic elements**
- ✓ **Low cost**
- ✓ **Direct tunable band gap of 1.0 ~ 1.5 eV**
- ✓ **Large absorption coefficient of 10^4 cm^{-1}**

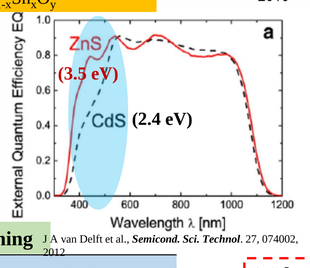


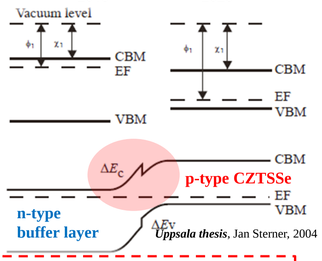
Zn(O,S) 、$Zn_xMg_{1-x}O$ 、$Zn_{1-x}Sn_xO_y$

White LED Spectra



Solar-powering the Internet of Things
Richard Haight, Wilfried Haensch and Daniel Friedman (July 7. 2016)
Science **353** (6295), 124-125. [doi: 10.1126/science.aag0476]





J A van Delft et al., ***Semicond. Sci. Technol***. 27, 074002, 2012

Uppsala thesis, Jan Sterner, 2004

lattice matching

Material	Lattice constant (nm)	Material	Lattice constant (nm)
CZTS	a=0.544	CZTSe	a=0.573
CdS	a=0.581	ZnS	a=0.542
ZnO	a=0.458	Mo	a=0.315

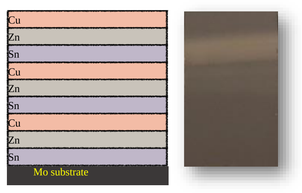
U. Hotje et al., Solid State Sci,2003, 5, 1259–1262Huakun Liu et al., Chem. Commun., 2010, 46, 1106-1108
T. Wada et al., Thin Solid Films, 2001, 387, 118-122

1. **Photogenerated carriers are blocked if ΔE_C > 0.4eV (Spike) resulting in a reduced FF.**
2. **If ΔE_C < 0 eV FF and V_{oc} are also reduced due to carrier recombination at the interface. (Cliff)**

0 < ΔE_C < 0.4eV

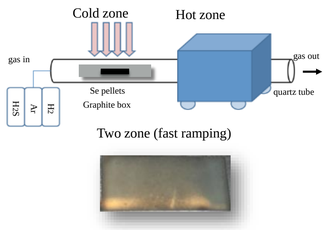
Experimental Method

1. Metal CZT precursor by sputter deposition



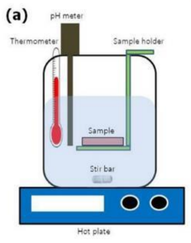
Metal precursor

2. Sulfo-selenization at 550°C



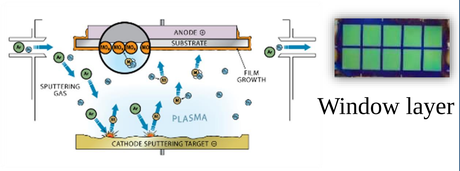
CZTSSe

3. Zn(O,S) buffer layer by chemical bath deposition (CBD) or atomic layer deposition (ALD)



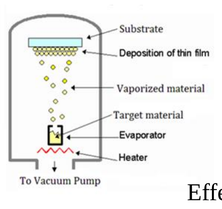
Zn(O, S)/CZTSSe

4. ZnO and ITO window layer by sputter deposition



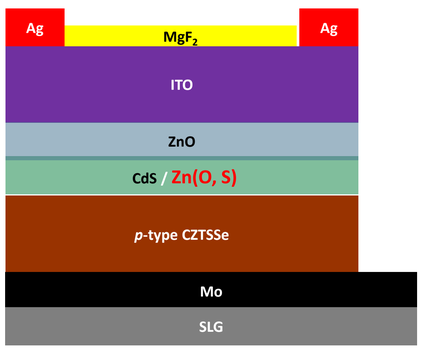
Window layer

5. Ag metal finger by thermal evaporation

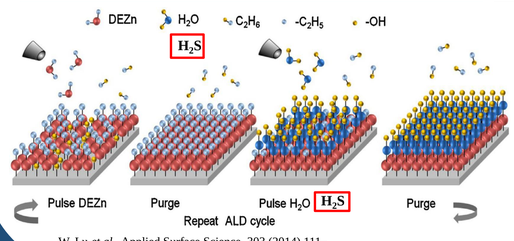


Devices

Total area 0.105 cm^2
Effective area 0.095 cm^2



Schematic diagram of ALD-Zn(O, S) growth mechanisms



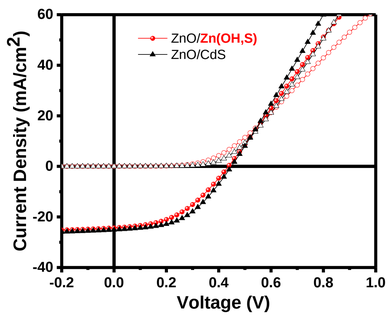
Zn(O, S):
1.Pulse H_2O
2.Pulse DeZn
3.Pulse H_2S
4.Pulse DeZn
5.Repeat cycle

Precursor of ALD:
- Self-limiting growth
- No decomposition
- No etching substrate

W. Lu *et al*., Applied Surface Science, 303 (2014) 111–117
Front Matter, in: Atomic Layer Depositionof Nanostructured Materials, Wiley-VCH Verlag GmbH & Co. KGaA, 2011,pp. I-XXXVI.

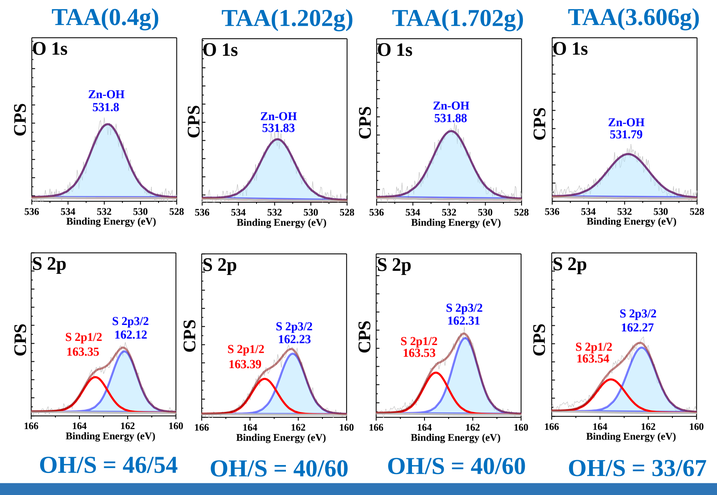
Result and Discussion

Zn(OH, S) of CBD by on CZTSSe IV curve (without MgF_2)

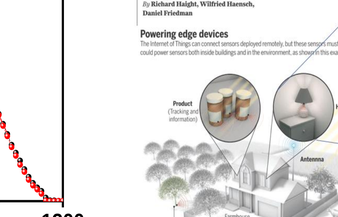


Device		Voc(V)	η(%)	FF(%)	Jsc (mA/cm²)	Rs(Ω. cm²)	Rsh (Ω. cm²)
ZnO/ CdS	Best cell	0.44	5.41	48.08	25.10	6.96	171.21
ZnO/ **Zn(OH, S)**	Best cell	0.43	4.68	44.09	24.32	7.93	141.63

XPS of Zn(OH,S) with different thioacetamide (TAA) concentration



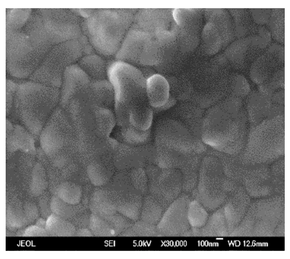
- **No signal of pure metal oxide** was found in **Zn(OH,S)** of CBD.
- From XPS data, **Zn(OH,S)** of CBD **can't change O/S ratio by changing the weight of thioacetamide**.



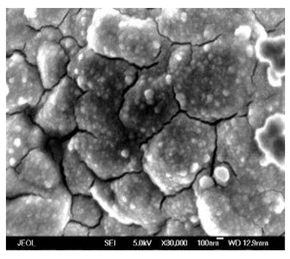
thioacetamide

SEM top view of CdS and Zn(OH,S)

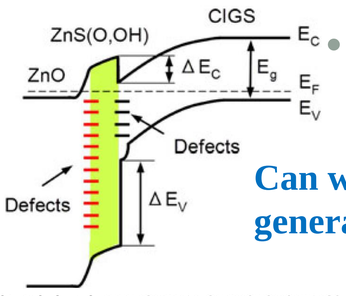
CdS on CZTSSe



Zn(OH,S) on CZTSSe



Small particles may be "**Zn(OH)**" 200 °C soft-baking for 10mins

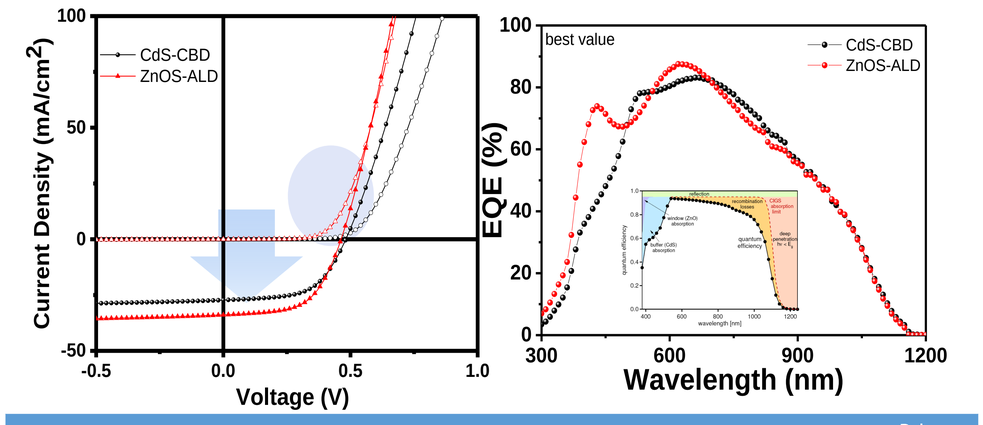


- These cracks may cause leakage current in devices.

Can we adjust O,S ratio , avoid ZnOH generation and cracks by ALD?

Tokio Nakada et al., IEEE JOURNAL OF PHOTOVOLTAICS, VOL. 3, NO. 1, JANUARY 2013

Zn(O, S) of ALD Device performance



J A van Delft et al., ***Semicond. Sci. Technol***. 27, 074002, 2012

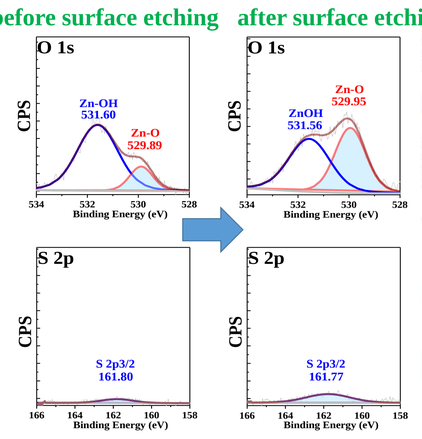
Device		Voc(V)	η(%)	FF(%)	Jsc (mA/cm²)	Rs(Ω. cm²)	Rsh (Ω. cm²)
CdS (CBD)	Best cell	0.48	8.07	58.51	28.70	3.99	237.27
	Mean	0.48±0.01	7.56±0.49	57.48±1.49	27.27±1.13	4.38±0.46	231.69±42.57
Zn(O, S) (ALD)	Best cell	0.46	9.77	58.06	36.07	3.15	206.70
	Mean	0.46±0	9.06±0.46	57.74±0.92	33.88±1.42	3.34±0.25	218.04±67.02

1. J_{sc} is improved from 28.7 to 36 (mA/cm²), PCE is improved from 8.0% to **9.7%, this is champion in the world.**
2. **Short wavelength region is enhanced** → band gap of CdS v.s ZnOS (2.4eV<3.5eV)

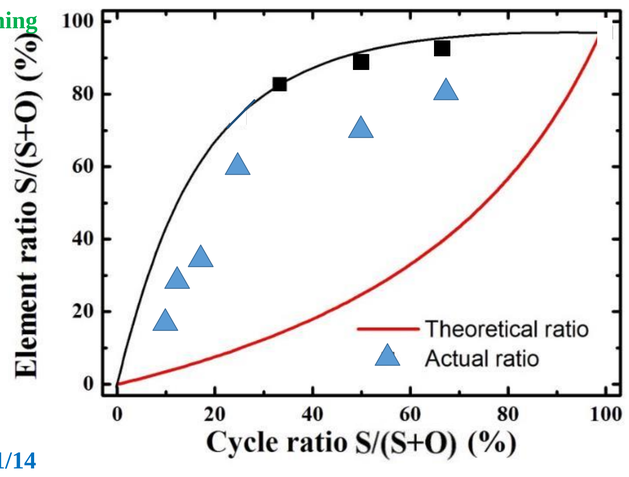
XPS of ALD Zn(OH, O, S)

Zn(OH,O,S)

before surface etching **after surface etching**



OH/O/S = 77/17/6 **OH/O/S = 45/41/14**



Cycle	XPS
O1 : S2	= 20:80
O1 : S1	= 30:70
O3 : S1	= 40:60
O5 : S1	= 65:35
O7 : S1	= 70:30
O9 : S1	= 82:18

1. We **successfully controlled the O/S ratio with the ZnO/ZnS cycle number by the ALD**
2. The **highest efficiency O/S ratio is 86:14**

Acknowledgement

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