Optimization of functional layers for kesterite thin film solar cells

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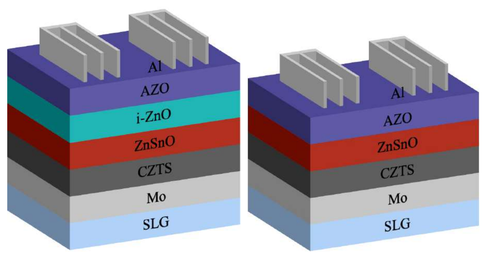
Earth-abundant kesterite thin-film, such as Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSn(S,Se)_4$ (CZTSSe), can be deposited with low-cost metodologies, even on flexible substrates. However, issues like inner defects, back surface recombination and a non-optimal band alignment with the toxic but conventionally used CdS buffer layer still limit the device performances. The use of an alternative material to CdS, such as ZnSnO (ZTO) and TiO_2, could improve charge transport and make the devices more sustainable. In our works, the growth on CZTS of ZTO [1] and TiO_2 [2] via Atomic Layer Deposition (ALD) was developed. Different stoichiometry, compositions and thicknesses were tested. Here we report also on the optimization of the back contact to design the kesterite solar cells grown by wet method [3] on flexible molybdenum foil.

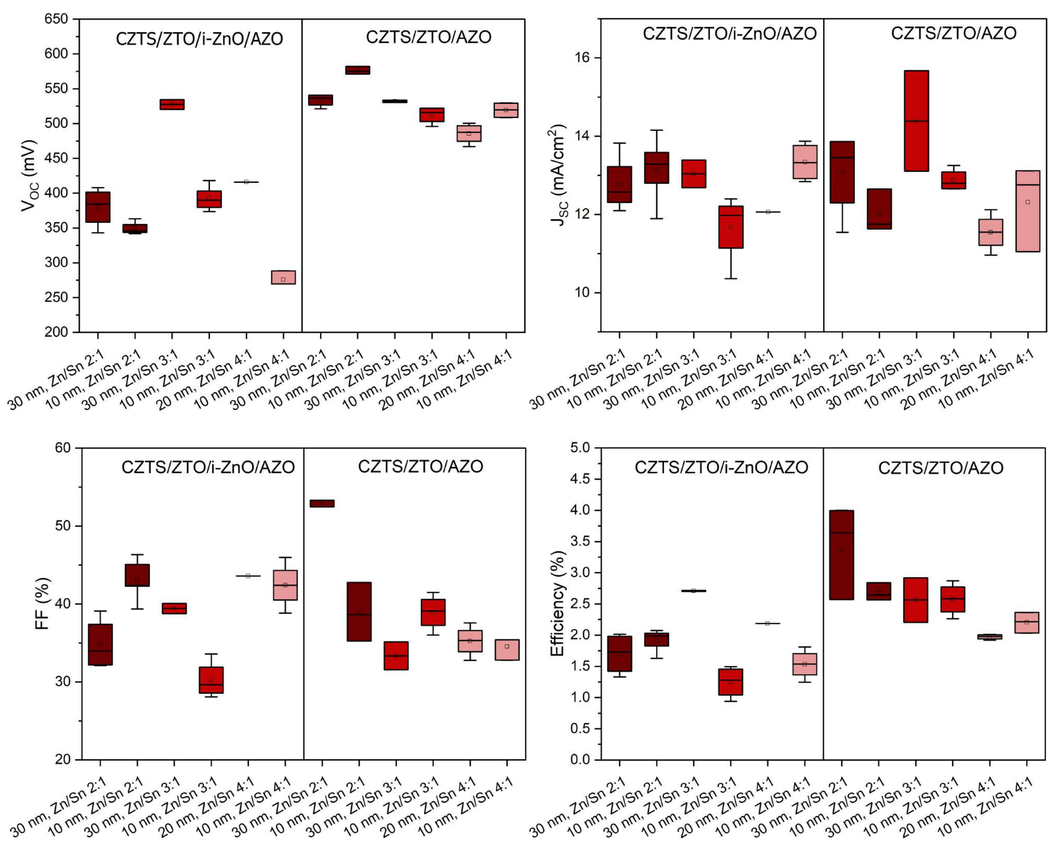
ZTO as alternative buffer layer

ZTO thin films, employed to complete the p-n junction, were prepared by thermal ALD. The deposition temperature was 150 °C. Diethylzinc [$Zn(C_2H_5)_2$, DEZ] and tetrakis-(diethylamino)tin(IV) [$Sn(N(CH_3)_2)_4$] were employed, respectively, as Zn and Sn precursors. Deionized water was used as co-reactant, and N_2 (99.9999%) as gas carrier. The ALD-cycle was composed of a sequence of DEZ/TDMASn:N_2:H_2O:N_2.



Two different architectures have been developed to investigate charge extraction. In both structures, layers of ZTO with three different compositions (Zn:Sn = 2:1, 3:1, 4:1) and with two different thicknesses (~30 nm and 10 nm) were analysed.

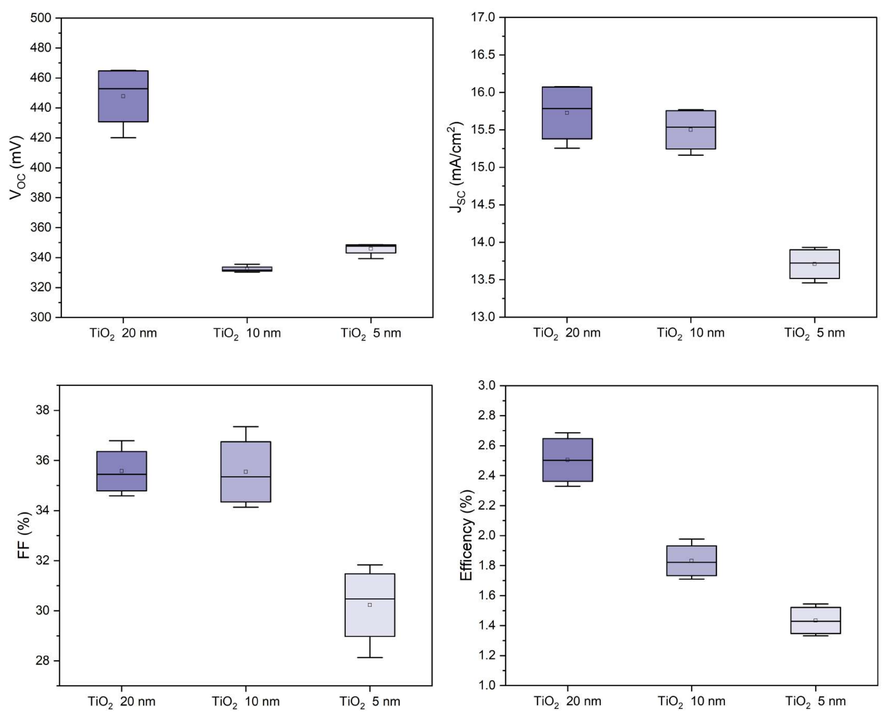
	ZTO 2:1	ZTO 3:1	ZTO 4:1	CdS
E_g (eV)	3.38	3.30	3.25	2.4

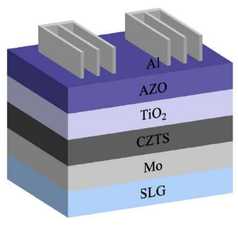


The most efficient device is the one with ZTO (Zn/Sn ratio 2:1) with 30 nm thickness and no i-ZnO.

TiO_2 as alternative buffer layer

TiO_2 thin layers have been deposited by O_2-plasma-ALD with a substrate temperature of 250 °C. Tetrakis-(dimethylamino)titanium(IV) [$(Me_2N)_4Ti$, TDMATi] was used as Ti precursor. N_2 was employed as carrier gas and for the line purge. The cycle was composed of a sequence of Ti:N_2:O_2-plasma:N_2. This process allowed the deposition of three different thicknesses (20, 10, and 5 nm).

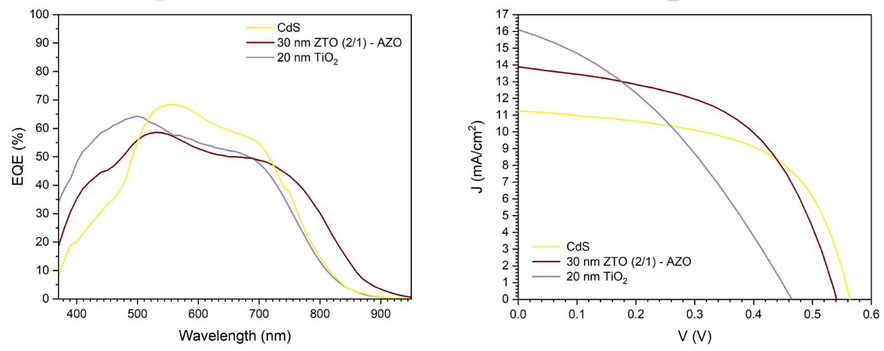




	E_g (eV)
TiO_2	3.2
CdS	2.4

We established a new record efficiency with the simplest possible cell architecture with 20 nm TiO_2.

Comparison between ZTO, TiO_2 and CdS



The CZTS/CdS's EQE reduction between 350 nm and 470 nm is mainly due to the CdS layer. This parasitic absorption is removed by replacing the CdS with both the ZTO and the TiO_2.

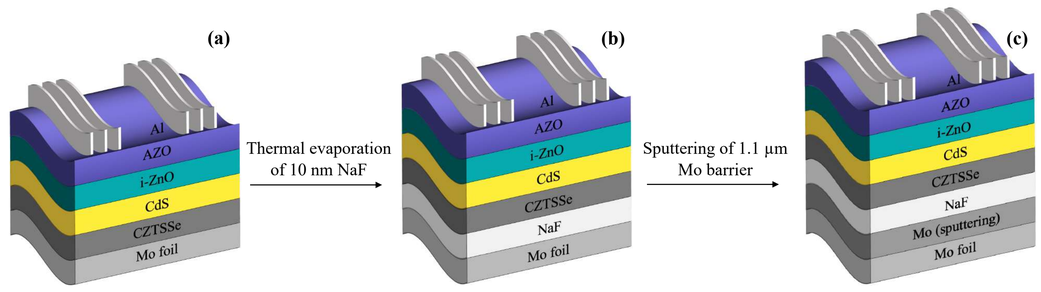
Buffer layer	Thickness (nm)	Top contact	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF (%)	η (%)
CdS	70	i-ZnO/AZO	563.4	11.2	58.3	3.9
ZTO (2:1)	30	AZO	540.9	13.9	53.3	**4.0**
TiO_2	20	AZO	466.0	16.1	37.0	2.8
			465.0*	16.5*	39.1*	3.0*
			480.0**	17.9**	42.8**	**3.7****

* 60' light soaking ** 60' light soaking + 1 year aging

The results obtained with CZTS/ZTO and CZTS/TiO_2 devices are comparable to the CZTS/CdS reference cells.

Mo foil as flexible substrate

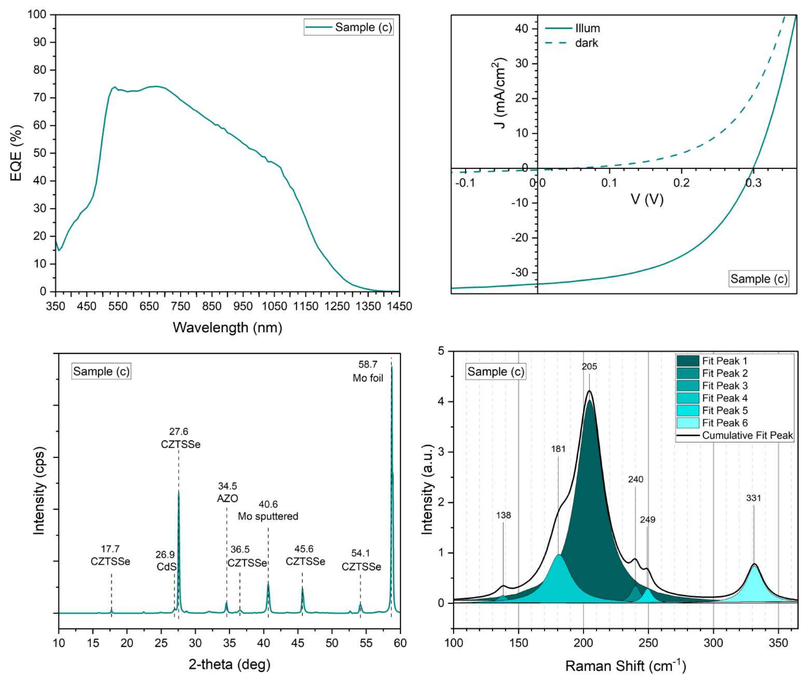
Mo foil is one of the most interesting substrates, thanks to its high temperature resistance, high conductivity and lack of metallic impurities. The functionalization of this substrate has been performed.
The deposition process of CZTSSe is based on the sol-gel technique with a direct blade-coating of the CZTS precursor solution, followed by a gelation process, a heat treatment in Ar atmosphere and a selenisation of the final stack in Ar atmosphere.



To reduce the process steps involved in the production of these devices, we are also testing and studying alternative methods to sodiate CZTSSe thin film, e.g. by introducing NaF directly into solution.

Sample	with 10 nm NaF	with 1.1 µm Mo barrier	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF (%)	η (%)
(a)	no	no	33.81	64.95	25.17	0.55
(b)	yes	no	31.74	86.42	27.52	0.75
(c)	yes	yes	299.49	33.21	50.74	**5.05**
Ref. on rigid SLG/Mo	no	no	322.33	40.27	38.31	4.97

NaF promotes, via sodium diffusion, the passivation of the CZTSSe grain boundaries. To reduce the diffusion of selenium towards the back contact and thus the formation of a thick layer of $MoSe_2$, which limits the charge extraction of the device, a more compact layer of Mo must be deposited by sputtering.



E_g = 1.1 eV

The efficiencies obtained are comparable to our devices on standard SLG rigid substrates.

XRD and Raman analysis show well-defined Kesterite peaks with no secondary phases.

[1] C. Gobbo *et al.* Energies **2023**, *16*, 4137.
[2] G. Tseberlidis *et al.* ACS Mater Lett **2023**, *5*, 219.
[3] G. Tseberlidis *et al.* Solar Energy **2020**, *208*, 532.

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