ALD-grown ZTO and TiO_2 as buffer layers in Cd-free kesterite solar cells

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Earth-abundant and environmentally friendly kesterite thin-film, such as Cu_2ZnSnS_4 (CZTS), can be deposited with low-cost methodologies. 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. The devices architectures and interfaces have been investigated and the role of i-ZnO window layer (conventionally used in CZTS/CdS devices) has been proved to be not only redundant, but also detrimental to the charge extraction. The resulting photovoltaic parameters are comparable with our CdS-based reference device.

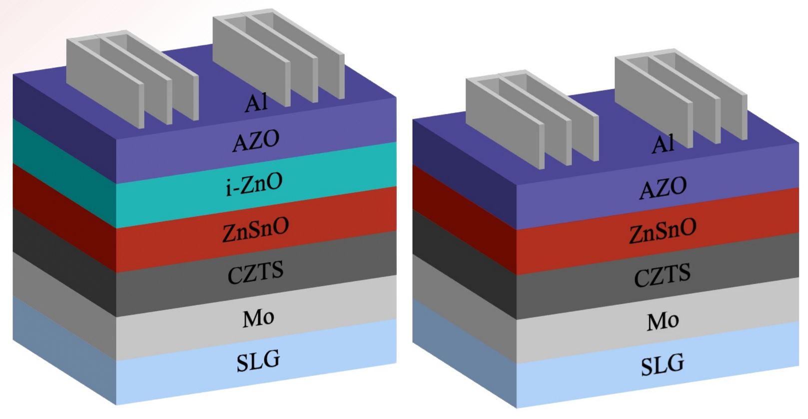
[1] C. Gobbo *et al.* Energies 2023, *16*, 4137.
[2] G. Tseberlidis *et al.* ACS Mater Lett 2023, *5*, 219.

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. The gas line from the precursor to the reaction chamber was heated to 100 °C. ALD process was based on the cyclic dosing of DEZ/TDMASn:N_2:H_2O:N_2.

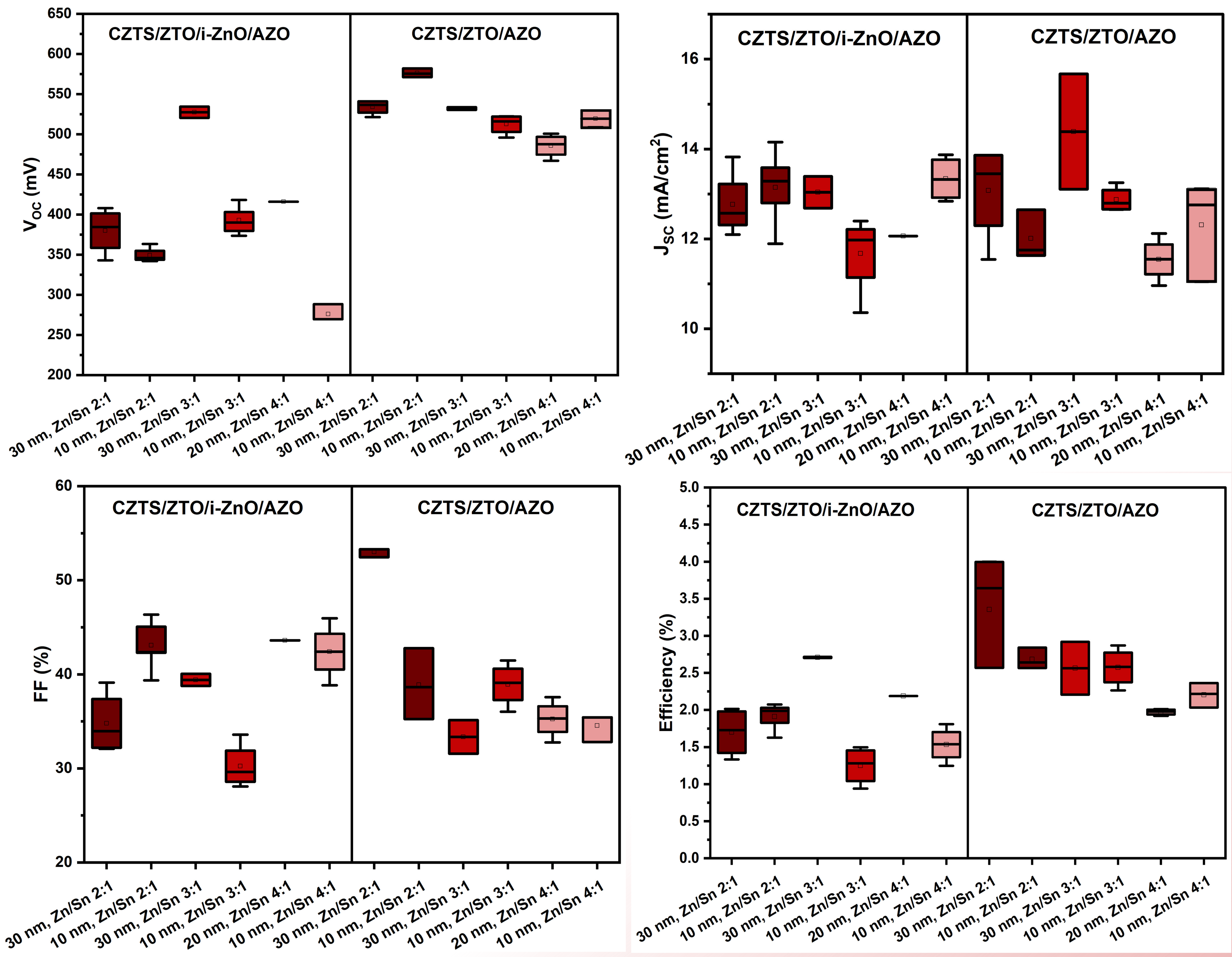
- Diethylzinc [$Zn(C_2H_5)_2$, DEZ] (maintained at 22°C) and tetrakis-(diethylamino)tin(IV) [$Sn(N(CH_3)_2)_4$] (heated to 75°C) were used as precursors of zinc and tin, respectively
- N_2 flux was used as gas-carrier and to purge reaction chamber
- H_2O (22°C) was used as co-reactant to oxidize metal precursors
- N_2 flux was used as gas carrier and to purge reaction chamber closing the cycle

The super-cycle scheme of the ZTO synthesis is composed of alternated cycles of ZnO and SnO_x with different ratios according to the desired composition.



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



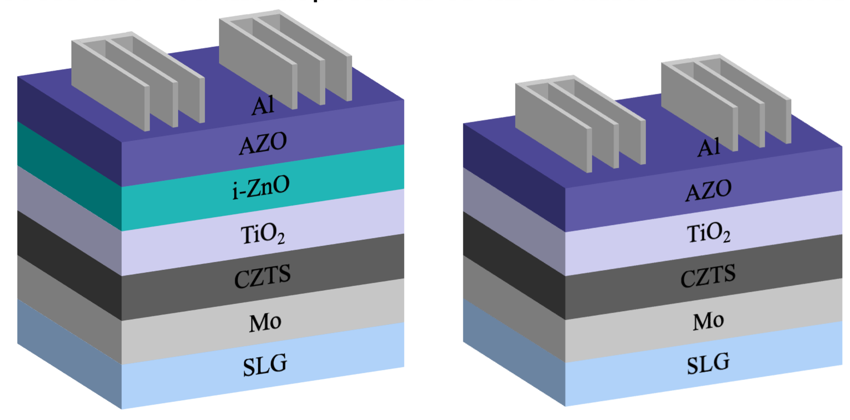
The most efficient device is the one with ZTO (Zn/Sn ratio 2:1) with 30 nm thickness and no i-ZnO.

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. The deposition temperature was 150 °C. ALD deposition cycle was Ti:N_2:O_2-plasma:N_2.

- Tetrakis-(dimethylamino)titanium(IV) [$(Me_2N)_4Ti$, TDMATi] (maintained at 67°C with gas line at 75°C) was used as Ti precursor.
- N_2 was employed as carrier gas and for the line purge.
- O_2 plasma was used to obtain TiO_2 film.
- N_2 flux was used as gas carrier and to purge reaction chamber closing the cycle

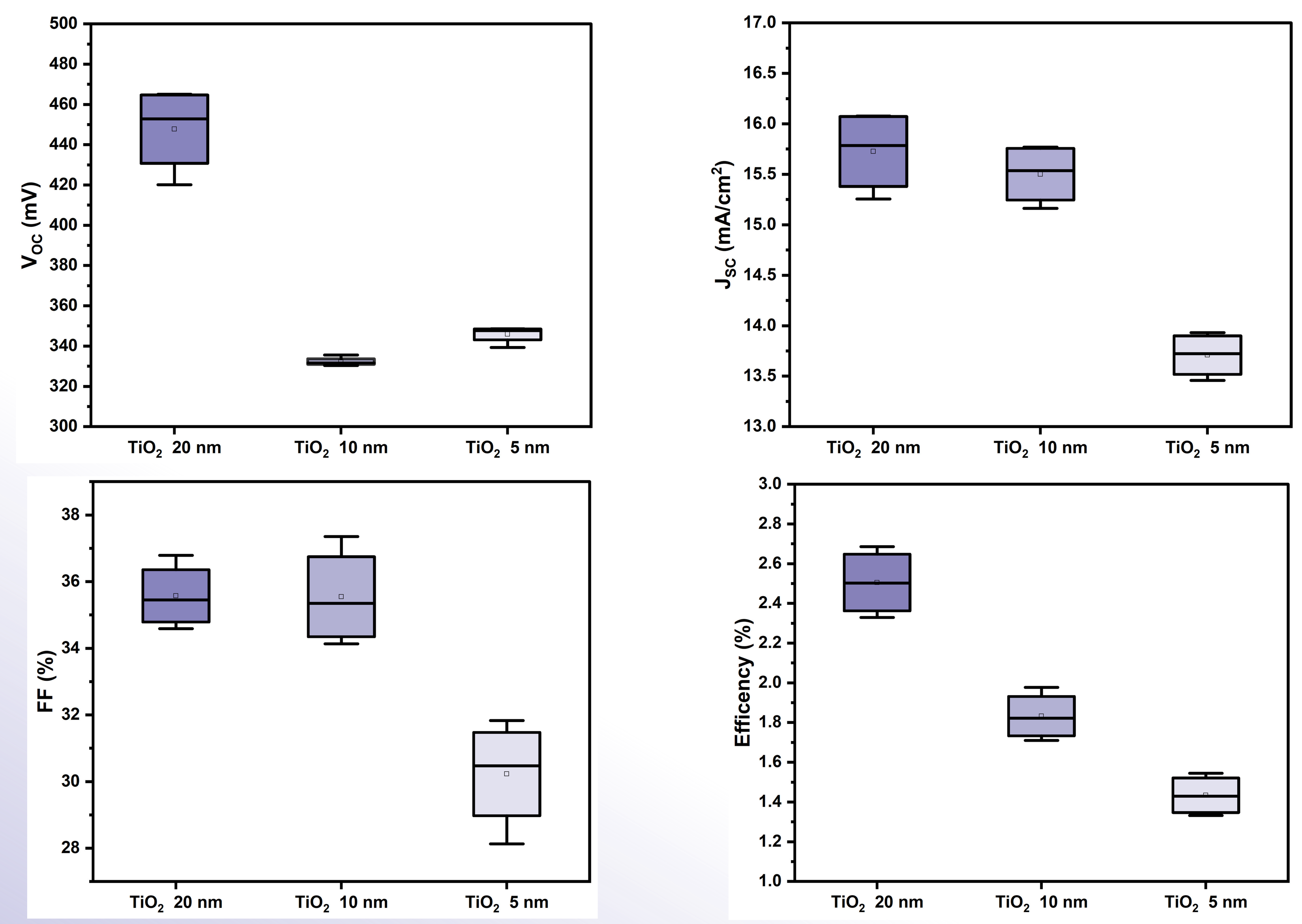
This process allowed the deposition of three different thicknesses (20, 10, and 5 nm).



	E_g (eV)
TiO_2	3.2
CdS	2.4

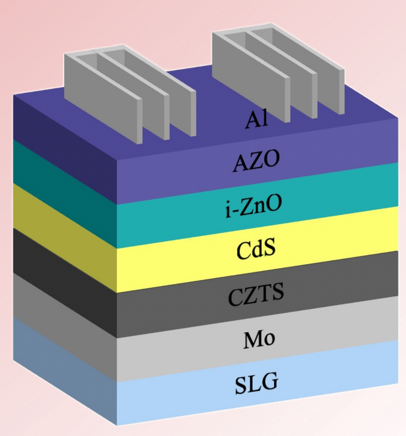
By using our standard cell architecture and substituting only CdS with TiO_2 (Mo/CZTS/TiO_2/i-ZnO/AZO/Al), no working solar devices were obtained, regardless of the TiO_2 thickness used.

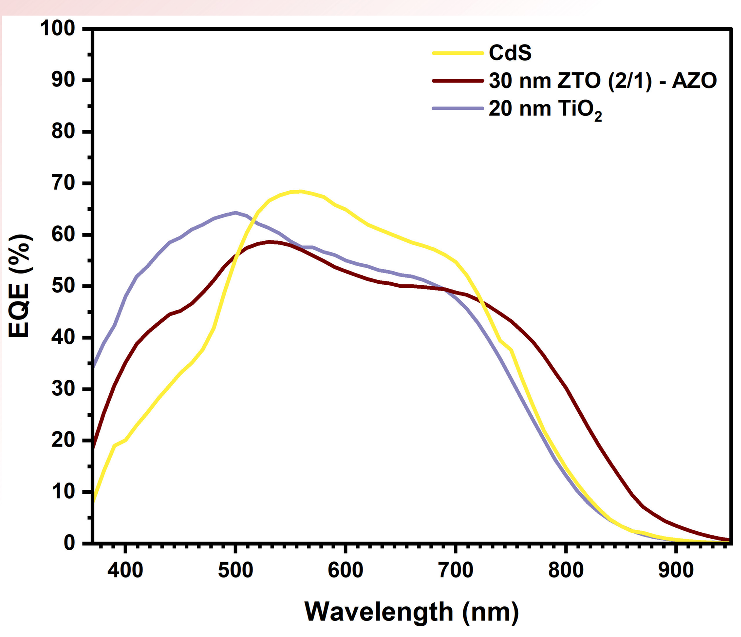
By removing the i-ZnO layer (Mo/CZTS/TiO_2/AZO/Al) working solar cells were obtained as shown below

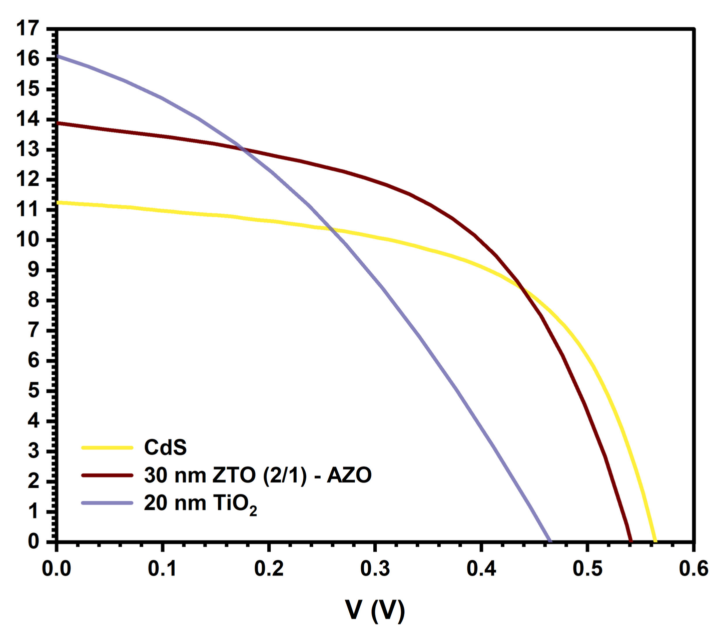


We established a new record efficiency with the simplest possible cell architecture with 20 nm TiO_2.

Comparison between ZTO, TiO_2 and CdS







CdS layer absorbs light in the range between 350 and 470 nm resulting in device efficiency drop. This parasitic absorption is removed by replacing CdS with both ZTO and 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.

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