Water-ethanol based sprayed photovoltaic solar cells.

BASQUE CENTER FOR MATERIALS, APPLICATIONS & NANOSTRUCTURES

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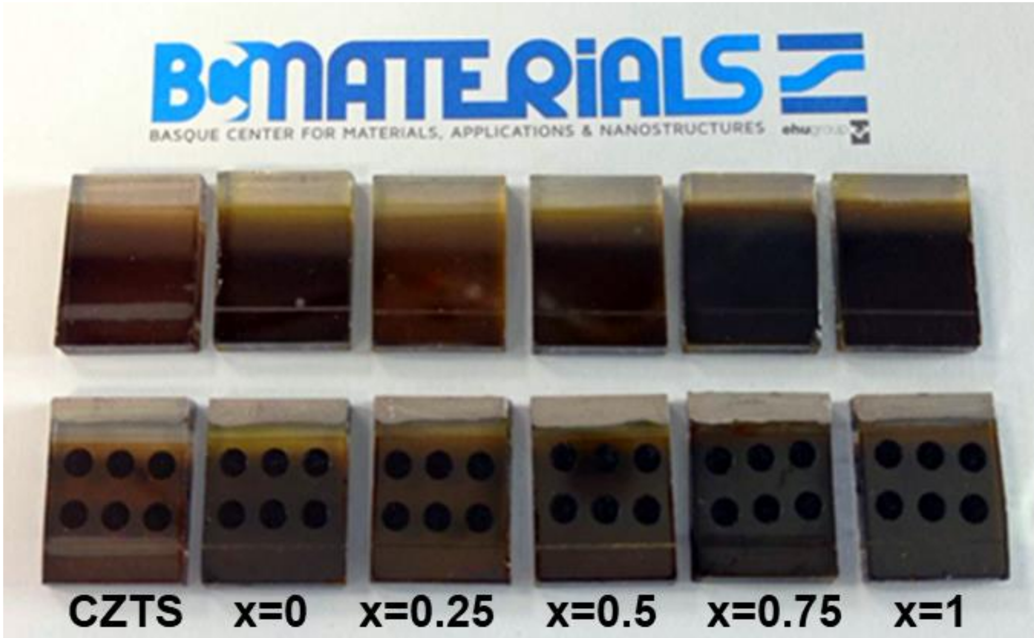
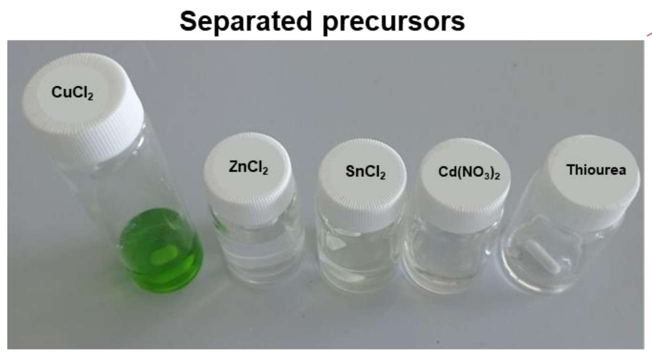
Abstract

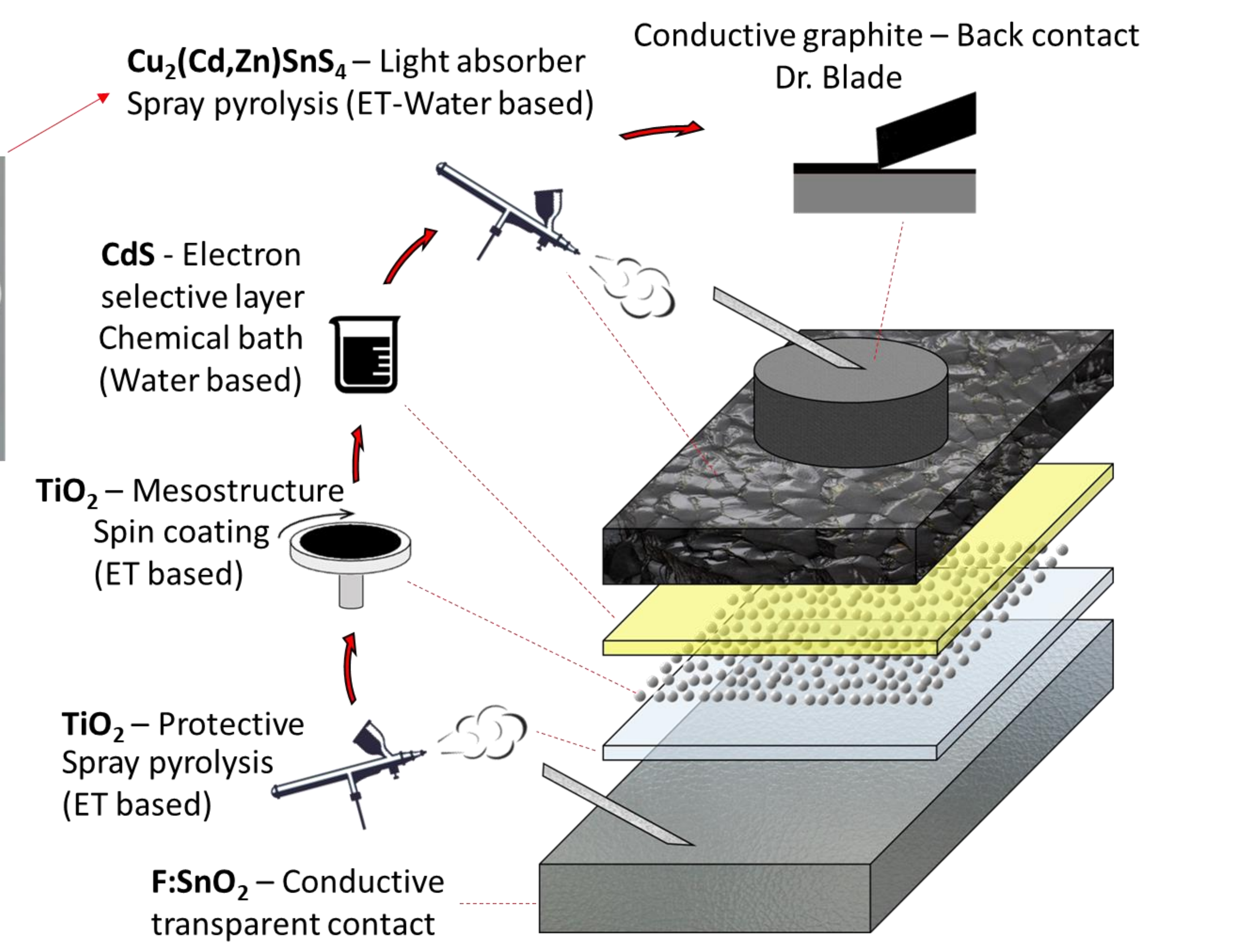
Chalcogenides materials have ideal properties as light absorber materials to fulfil the next generation of large production photovoltaics. They are composed of abundant raw materials, with low toxicity, high stability, can be synthesised at low to moderate temperatures, and required low film thickness to work efficiently. Developing a superstrate architecture, based on an FTO/TiO_2 electrode, allows new ways of engineering the formation of the thin film. This is in line with the motivation of reducing the use of scarce elements, while at the same time, it brings the possibility for new ways of improvements as absorber layer due to the sturdiness of the electrode. However, the layer deposition and formation usually requires sophisticated equipment, increasing the cost. **It is possible to use green and low-cost wet chemistry deposition methods to prepare chalcogenide films for photovoltaic solar cells?** We develop a spray solution to prepare $Cu_2(Cd_x,Zn_{1-x})SnS_4$ light absorber materials and test it in photovoltaic solar cells fully based on water and ethanol.



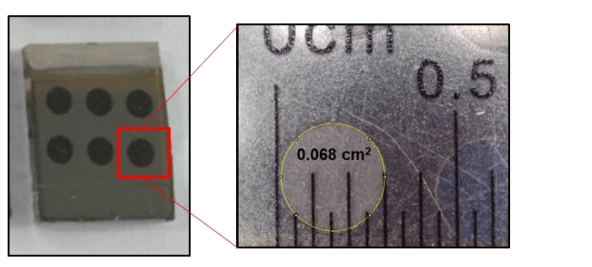
Methods

Separated precursors





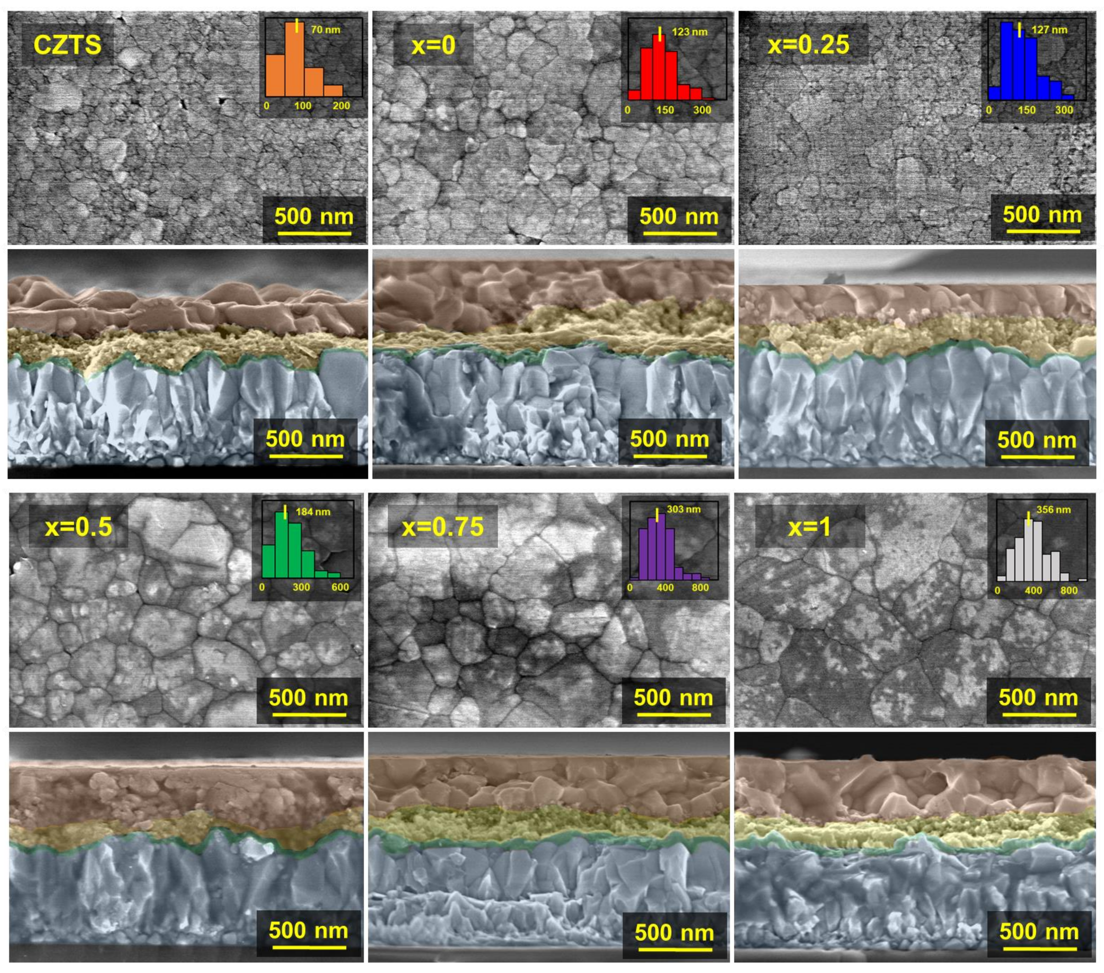
Active area defined by the graphite



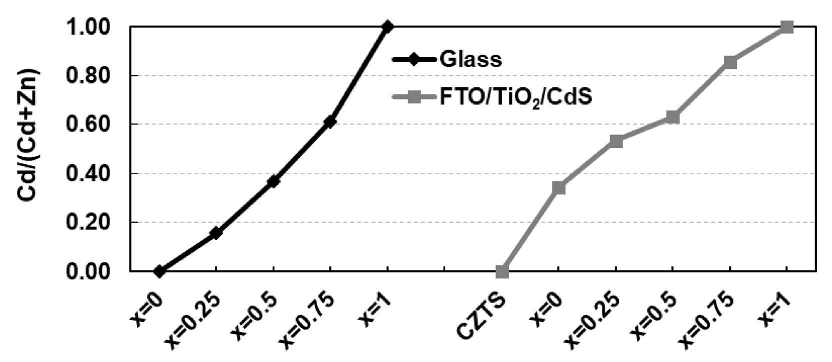
Film characterization

SEM top view of the absorber layer, indicating the crystal size. A bigger crystal size reduce the charge recombination in the inter-grains defects. High Cd content improves the size.

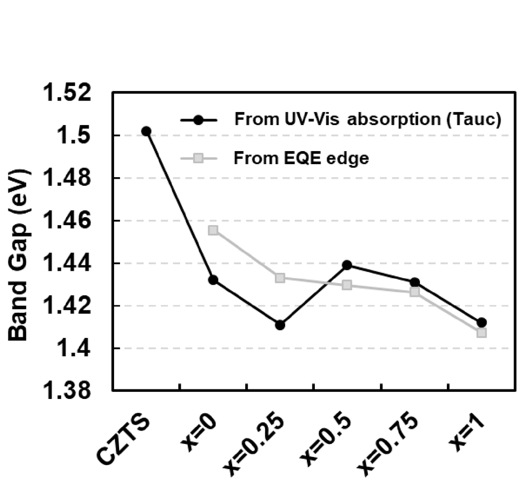
SEM cross-sectional view of the photovoltaic cells. The different films are identified as FTO (blue), TiO_2 (green), mesoporous TiO_2 and CdS (yellow) and $Cu_2(Cd_x,Zn_{1-x})SnS_4$ (red)



Elemental analysis of the absorber film by EDX. The Cd/(Zn+Cd) composition is close but higher to the precursors ratio used, but lower when deposited on glass.

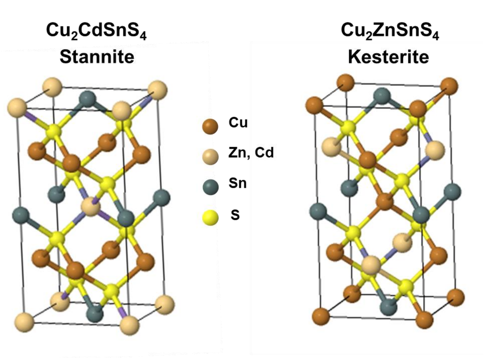


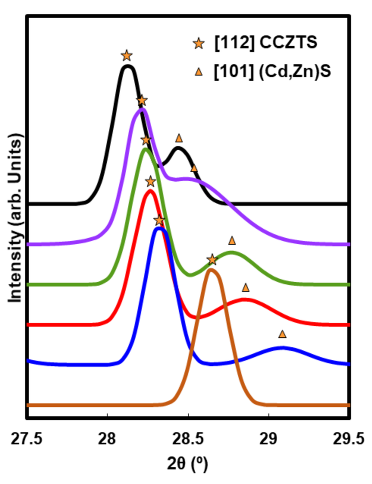
The band gap this materials change with composition. Very close to ideal values (1.36 eV) for PV applications.

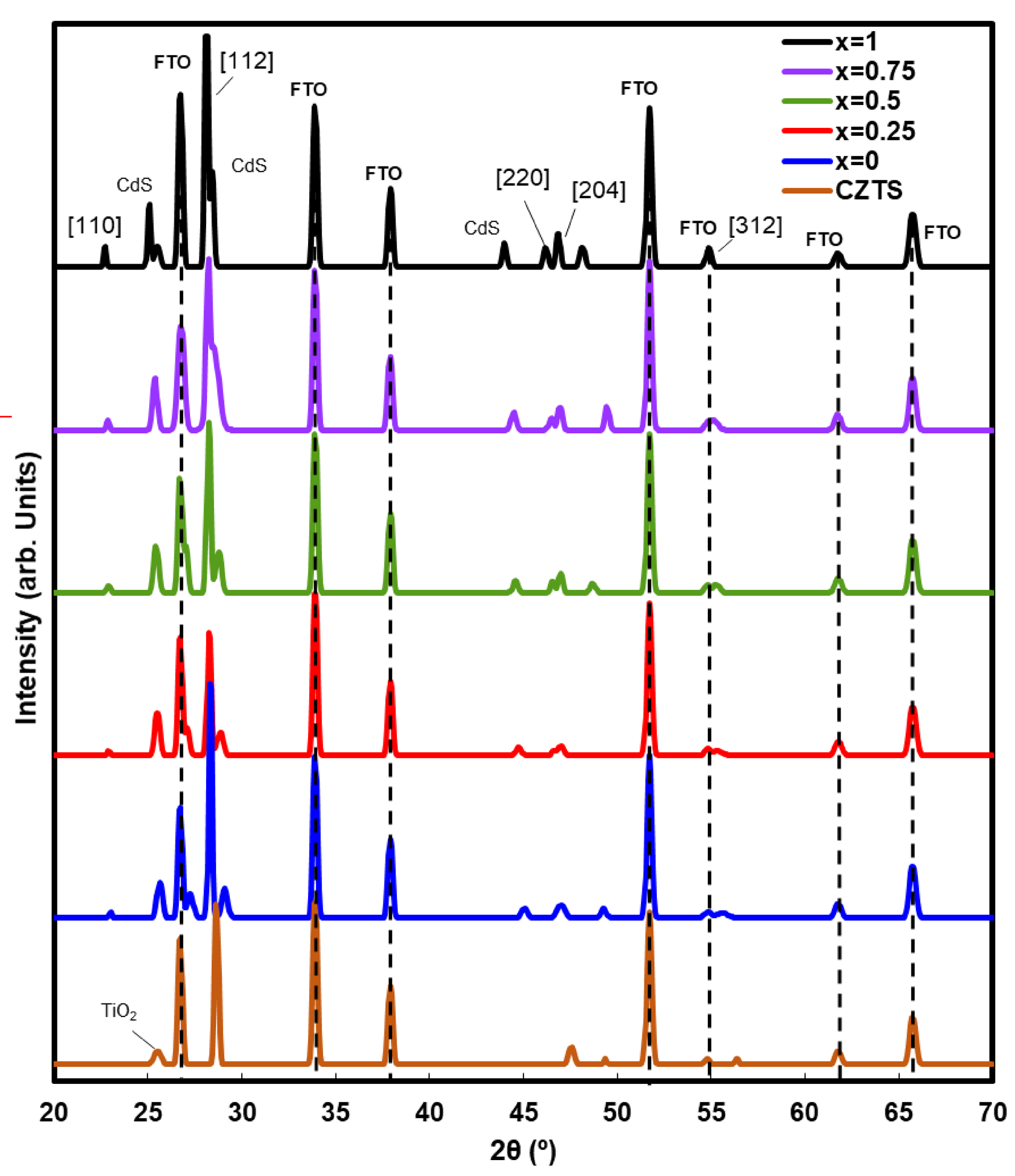


XRD analysis reveals a progressive change in the crystal structure. The structure of Cu_2CdSnS_4 is stannite, while Cu_2ZnSnS_4 is kesterite.

A secondary phase of (Cd,Zn)S with wurzite structure is identified, due to Zn diffusion on the CdS film, with a Cd-Zn ratio proportional to the precursors.





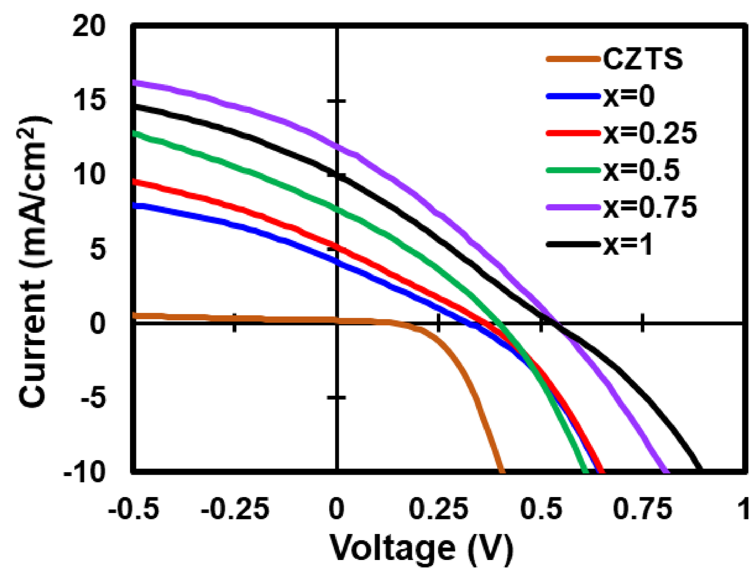


Solar cell characterization

Under illumination

J-V curve under 1 Sun AM1.5 (1000 W/m²) shows the photovoltaic properties. At the maximum power point, the light conversion efficiency can be calculated.

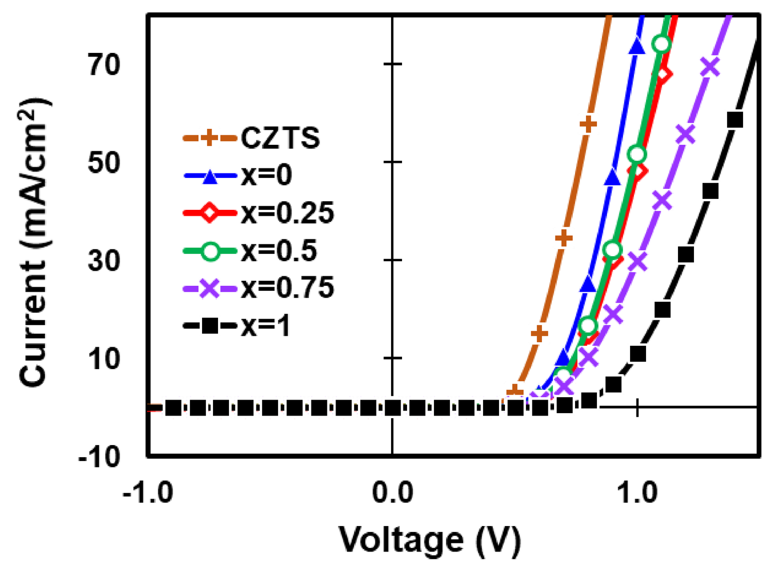
The best efficiencies are reach with x=0.75 and x=1 compositions.



Current voltage in dark

Without illumination, the solar cells behaves as a *PN* junction forming a diode. The diode factor, series and shunt resistances can be extracted.

A higher knee voltage indicates a better junction with less recombination.
Shunts under reverse current are very low.

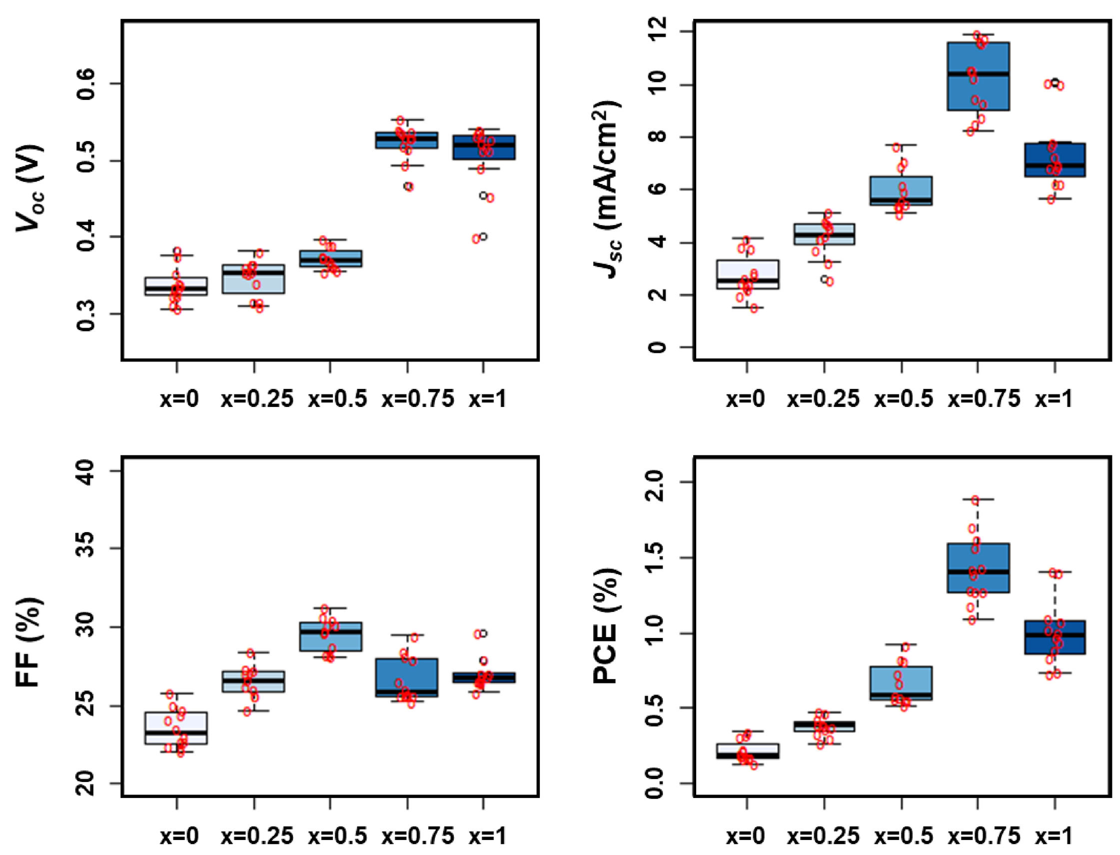


Statistics of solar cells performance

The main PV characteristics under 1 Sun illumination over 12 cells for each condition.

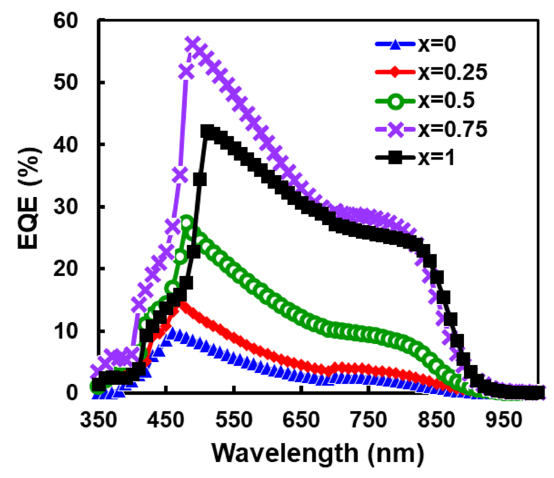
Statistics over many cells ensures the reproducibility of the process and results.

The increase of Cd in the composition results in with better J_{sc} and V_{OC}. We associated this with the secondary phase (Cd,Zn)S. CdS has better electric conduction than ZnS.



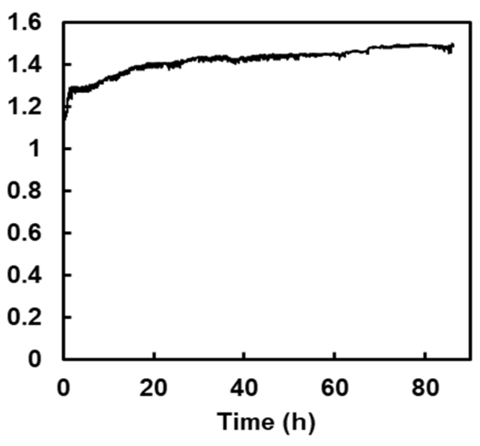
External quantum efficiency (EQE)

Efficiency of photon-to-electron conversion for every light wavelength. Parasitic absorptions, band-gap and internal processes can be elucidated. All samples have more stability wavelengths, but it is higher for x=0.75 and x=1.



Max power point tracking stability

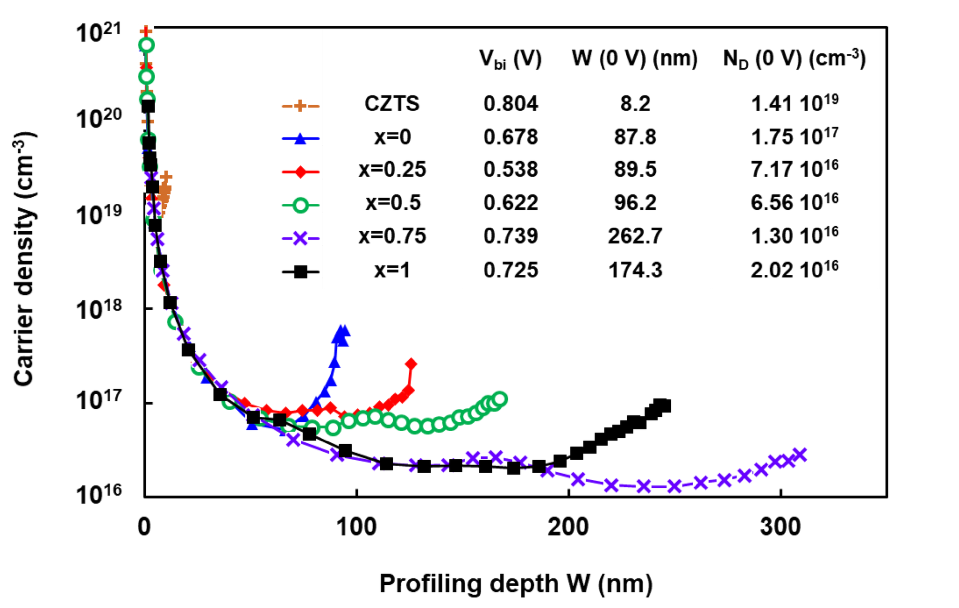
Solar cell must last for many years to be useful. The sample x=1 have the best stability under continuous illumination for more than 80 hours, without showing any degradation on the efficiency.



Capacitance Voltage

Measuring the capacitance of the PN junction is used to calculate the density of free carriers and the thickness of the junction by the Mott-Schottky equations.

A low carrier density indicates less defects, and a thick depletion width improves the photovoltaic effect.



	V_{oc} (V)	W (0 V) (nm)	N_D (0 V) (cm^{-3})
CZTS	0.804	8.2	$1.41\ 10^{19}$
x=0	0.678	87.8	$1.75\ 10^{17}$
x=0.25	0.538	89.5	$7.17\ 10^{16}$
x=0.5	0.622	96.2	$6.56\ 10^{16}$
x=0.75	0.739	262.7	$1.30\ 10^{16}$
x=1	0.725	174.3	$2.02\ 10^{16}$

Conclusions

- Photovoltaic solar cells made of thin films were prepared by spray pyrolysis using only water-ethanol based solutions using simple techniques, than can be prepared in large scale without sophisticated systems.
- The alloy $Cu_2(Cd_x,Zn_{1-x})SnS_4$ was studied, and show good optoelectronic properties for solar cells in superstrate architecture. Band-gap, crystallinity and secondary phases are improved for high Cd content.
- An almost 2 % of photovoltaic efficiency is demonstrated with sprayed $Cu_2(Zn_{0.25},Cd_{0.75})SnS_4$, and a good stability with more than 1.4 % is get for Cu_2CdSnS_4.
- This materials are compatible with flexible solar cells, low power devices, and are robust under extreme environmental conditions. Still a lot of room for the efficiency improvement!

Acknowledgements

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