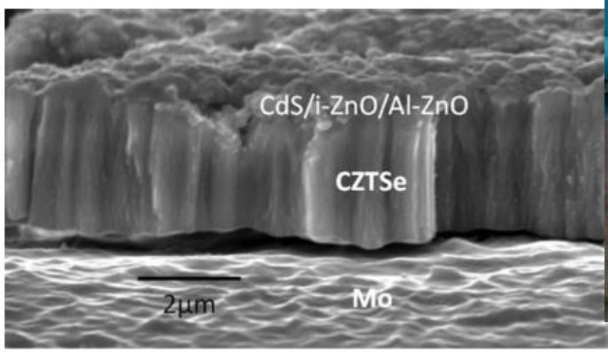
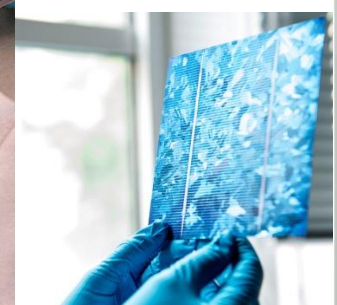
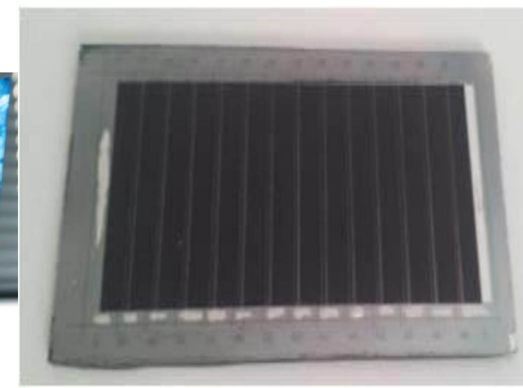
Earth-abundant chalcogenide thin film for PV application: the activity of MIB-SOLAR center at University of Milano-Bicocca

Simona Binetti

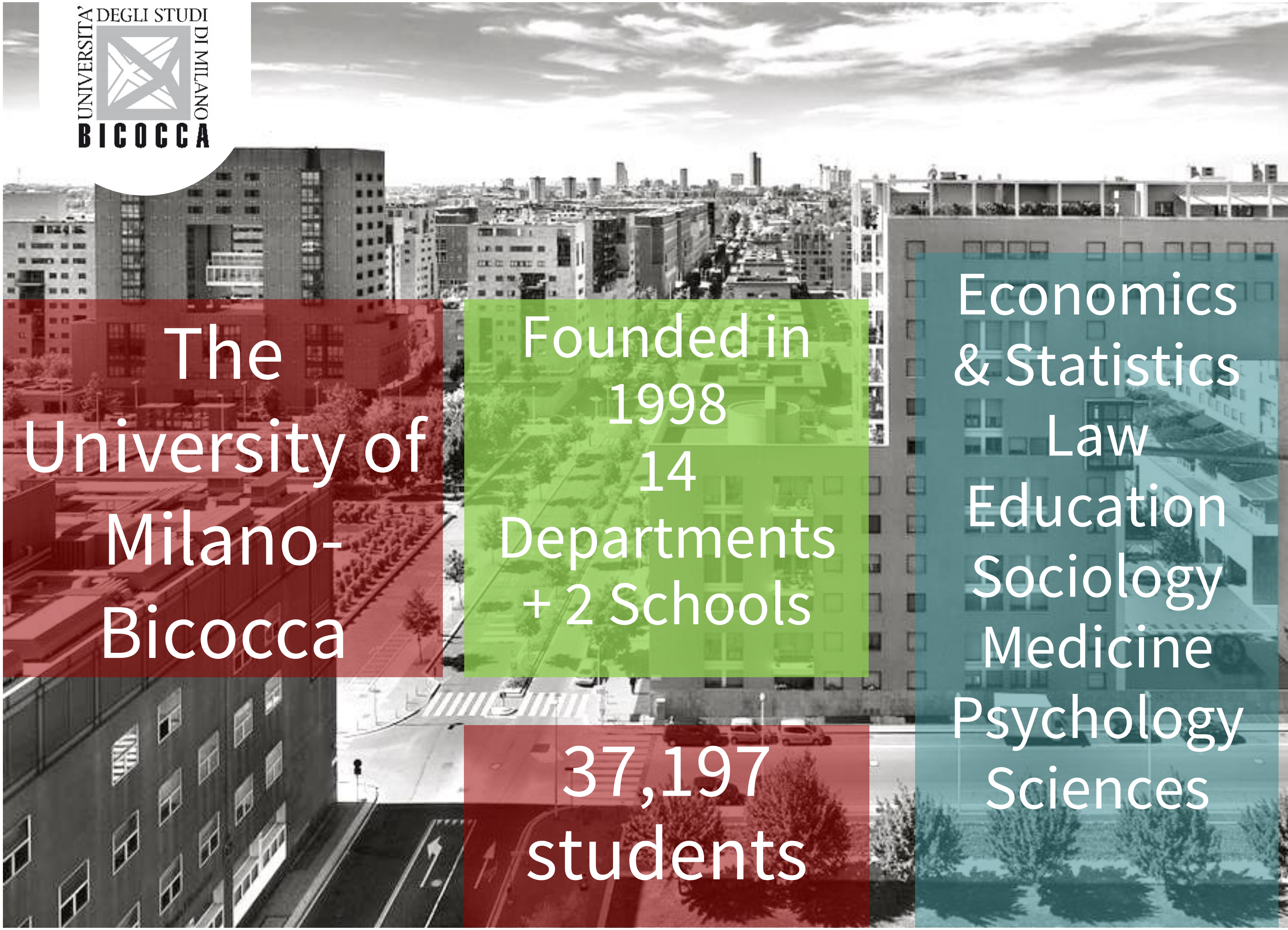


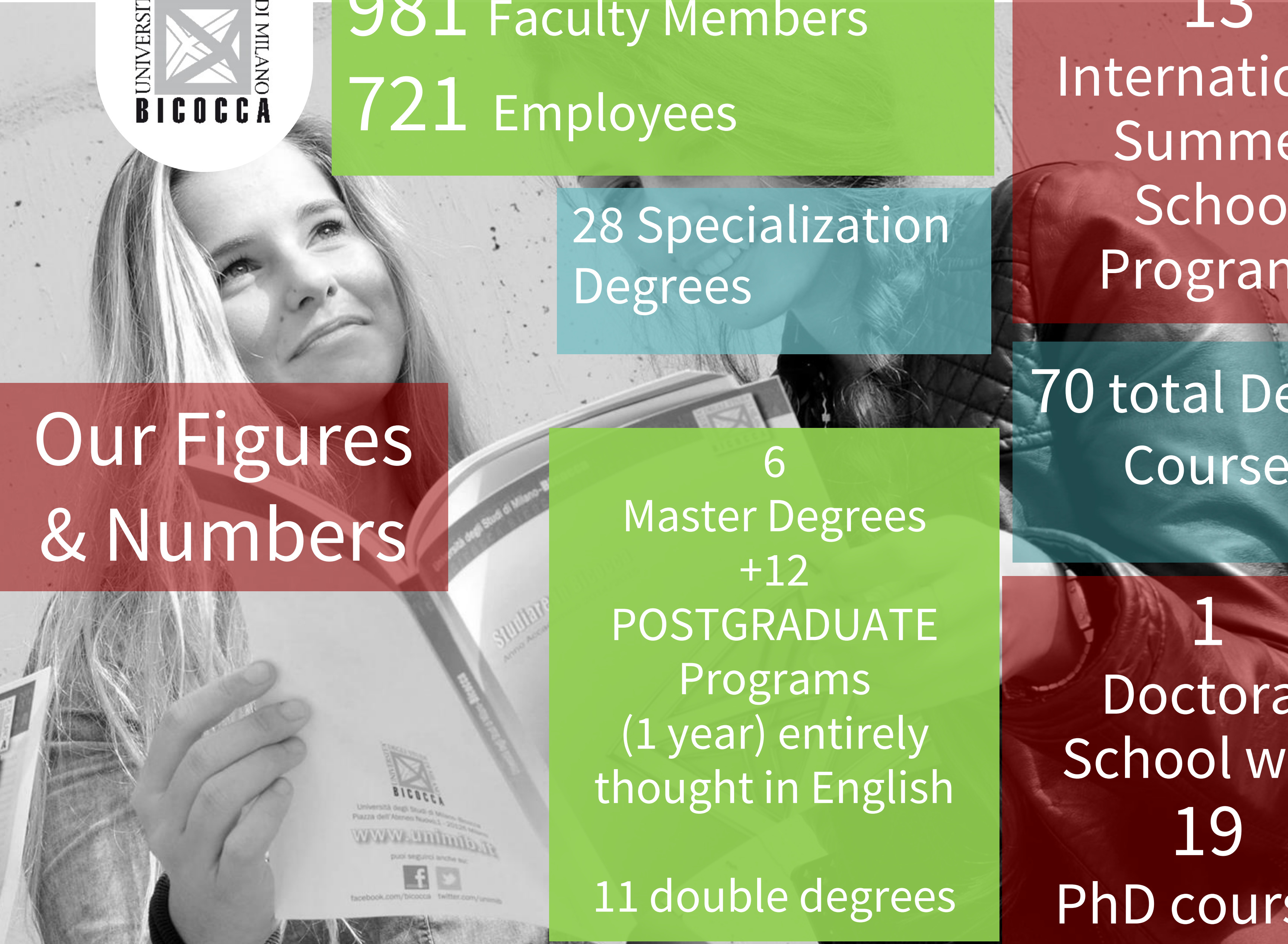




The University of Milano-Bicocca

www.unimib.it

S.Binetti, Sydney 27th November 2019


UNIVERSITA' DEGLI STUDI DI MILANO
BICOCCA
The University of Milano-Bicocca
Founded in 1998
14 Departments + 2 Schools
37,197 students
Economics & Statistics
Law
Education
Sociology
Medicine
Psychology
Sciences



Our Figures & Numbers

981 Faculty Members

721 Employees

28 Specialization Degrees

13 International Summer School Programs

70 total Degree Courses

6
Master Degrees
+12
POSTGRADUATE Programs
(1 year) entirely thought in English

11 double degrees

1
Doctoral School with
19
PhD courses


UNIVERSITA' DEGLI STUDI DI MILANO BICOCCA
2nd in The National ANVUR ranking on Big Universities
THE ONE HUNDRED FIFTY
Times Higher Education
Rank N. 82
Among universities less than 50 years' old
What we achieved in 20 years
8 Dep.ts are benchmark of EXCELLENCE
3 in Lombardy for number of students

UNIVERSITÀ DEGLI STUDI DI MILANO BICOCCA

Campus MILANO

Marine Research and High Education Center (*#MaRHE Center*)

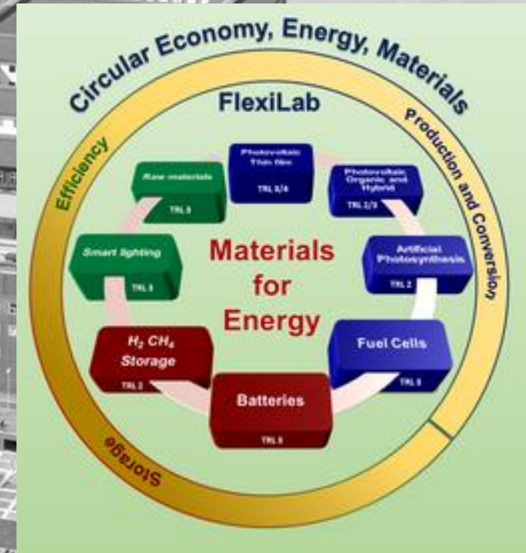
Campus Maldives

environmental sciences , marine biology, science of tourism , human geography

http://www.marhe.unimib.it/

Department of Material Science

www.mater.unimib.it



Bachelor and Master Degrees:

- Materials Science
- Chemistry
- Optical Technologies
- Phd in Materials Science

In a competitive funding from the Italian Government the SdM was granted to the best 180 Italian Departments :
The project "Electrical Power and Energy Vectors from Renewable Sources " FLEXILAB; research activity on materials for a sustainable energy cycle.

MIB-SOLAR CENTER @ UNIVERSITY OF MILANO BICOCCA

Base Research

FABRICATION OF CELLS AND MODULES

To support SME companies: from Research to Market

Founded in 2010

Mission

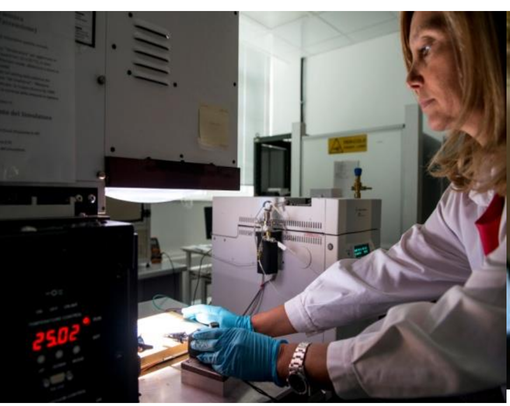
PV center allowing to pass from an academic research to the setup of a prototype devices

fully equipped synthesis and characterization labs

100 m^2 ISO 7 clean room

FULL MEMBER OF

EERA
European Energy Research Alliance



MIB-SOLAR equipment

Material Characterization

Raman spectroscopy

FT-IR, FT-NIR

HR Scanning Electron Microscopy (EBIC)

X-ray Diffraction

Photoluminescence spectroscopy

UV-Vis/NIR spectroscopy

Hall measurements

Material and cell preparation

CIGS, CZTS and DDSC cells and mini-module

innovative growth process for CIGS

sputtering system

glove box

laser scribing machine

Hotplates, furnaces

screen printers

UV-ozone cleaners

Devices Characterization

solar simulators up to 6 x 6 inches

I/V characterization

Internal and external quantum efficiency

light soaking chamber for cell ageing stability studies

electrochemical impedance spectrometer

MIB-SOLAR RESEARCH TOPICS

Inorganic Photovoltaic devices

- Silicon
- Inorganic thin film (CIGS – CZTS)

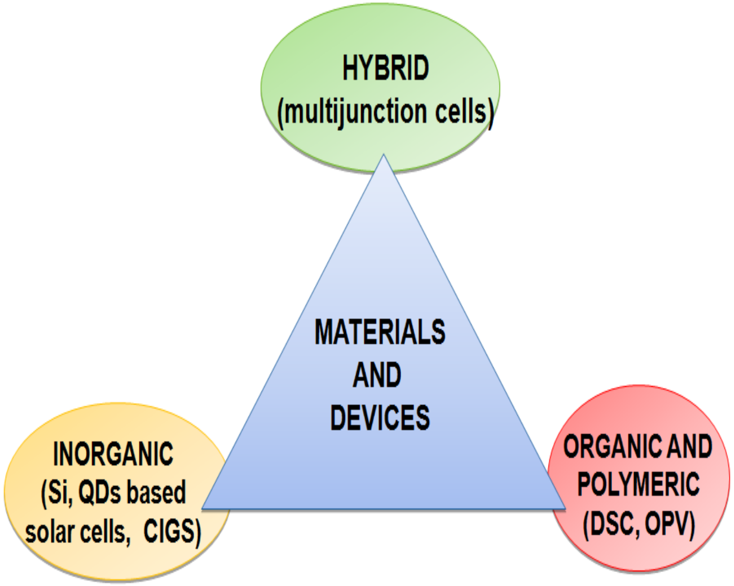
Organic Photovoltaic devices

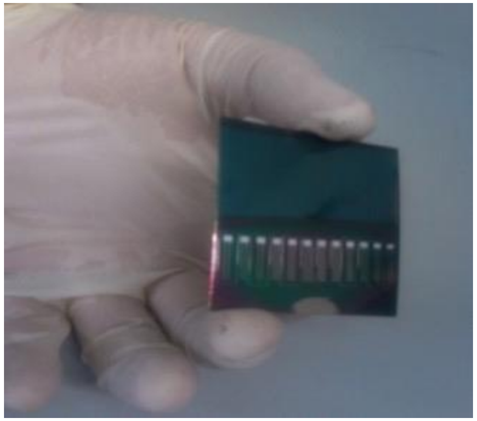
- Dye sensitized solar cells

Solar fuels (artificial photosynthesis)

- Production of Hydrogen

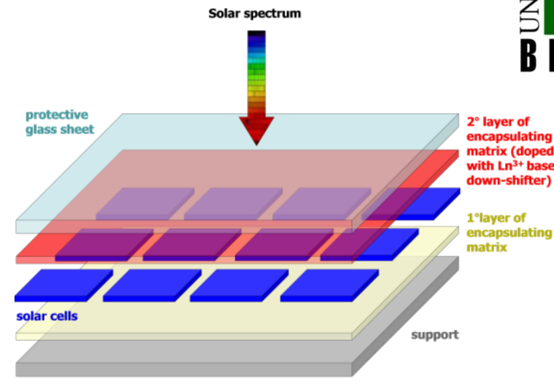
Purification of Biogas





Inorganic Photovoltaic materials and devices

S.Binetti



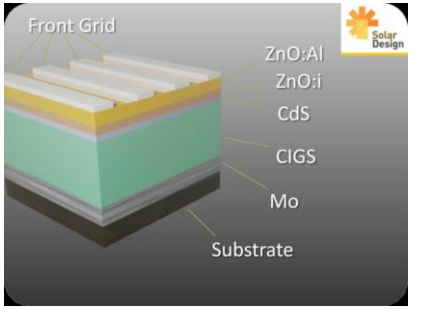
Silicon solar cells

Since 1991 involved in EU project on silicon solar cells

mc –Si: role of defects (dislocations, grain boundaries)

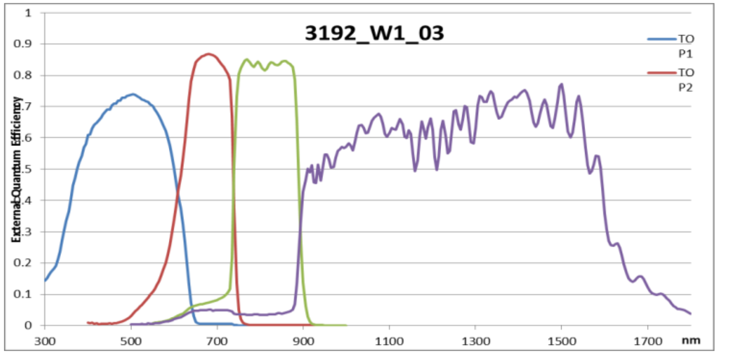
Metallurgical silicon : defect and compensation effect

Light harvesting, (EVA doped with Eu complexes)



Inorganic thin-film technologies: growth and characterization

- $Cu(In,Ga)Se_2$
- CZTS
- CMTS

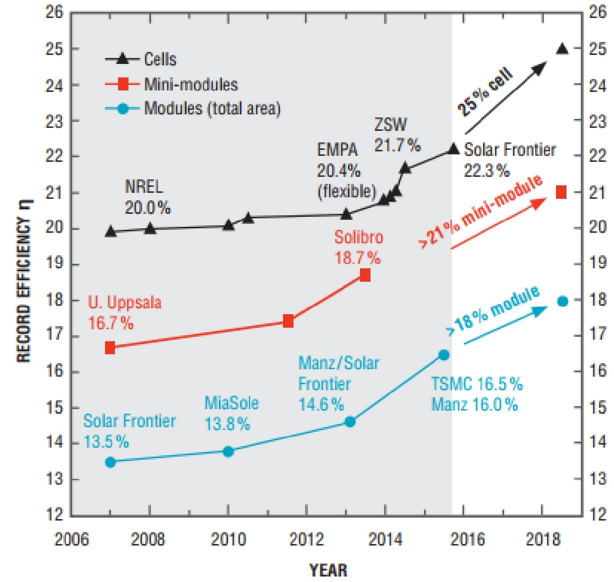


III-V based multijunction solar cells : characterization

- AlInGaP and AlInGaAs for 4 junction devices for space application (CESI Spa) (h=34%)
- Integration of triple junction on silicon

Chalcogenide thin film solar cells

✓**$Cu(In,Ga)Se_2$ (CIGS)** solar cells are very well positioned in the PV technologies with present record efficiencies 22.9 % for small cells and 16.5 % for production size modules
(Total world-wide CIGS production capacity is ~2 GWp/a)



✓Diversification of production and design of CIGS modules
-CIGS glass-glass products for BIPV
-Flexible and light weight CIGS modules for PIPV


image: Manz AG

http://cigs-pv.net/white-paper-for-cigs-thin-film-solar-cell-technology/

✓CIGS can be used as bottom cell in tandem devices (η> 30 %)

✓Lower temperature coefficients, higher shading tolerance , a good low light performance are also key CIGS properties, plus a short energy payback time

CIGS technology: open questions

•Complexity of the absorber layer (significant challenges for uniform film properties across a large area)

•the knowledge of the absorber layer is not sufficient

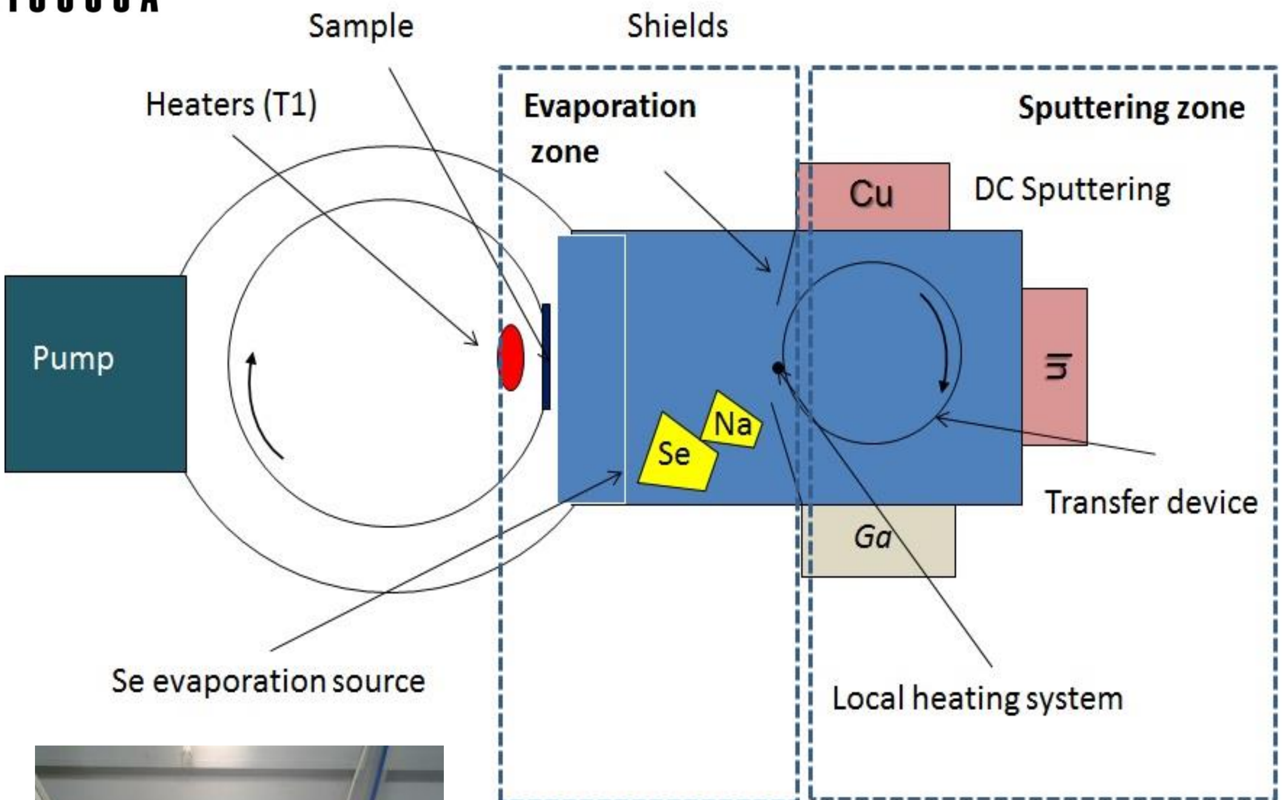
•Current production should increase

•So far being able to produce solar panels at prices that can compete with polycrystalline or cadmium telluride panels has not been possible.

•New deposition system for an easy scale up roll-to-roll configuration (for flexible substrate) is necessary

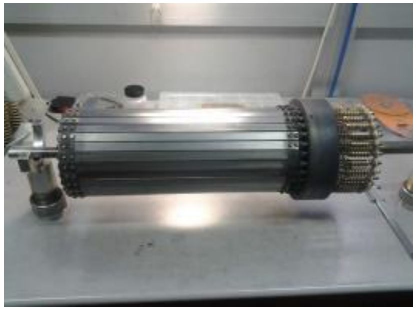
Most CIGS solar cells are nowadays produced using a co-evaporation technique that involves vacuums and can be costly and time-consuming.

Cu(In,Ga) Se_2 @ MIB-SOLAR: A new hybrid sputtering /evaporation process *



1. The metal precursors are sputtered on rotating <u>transfer devices</u>
2. Then the metals are evaporated on the substrate by local heating elements in a Se atmosphere
3. The sputtering and the evaporation processes continue up to the desired thickness is reached
4. Cooling steps in the presence of Se

PCT European Appl., EP 13425019

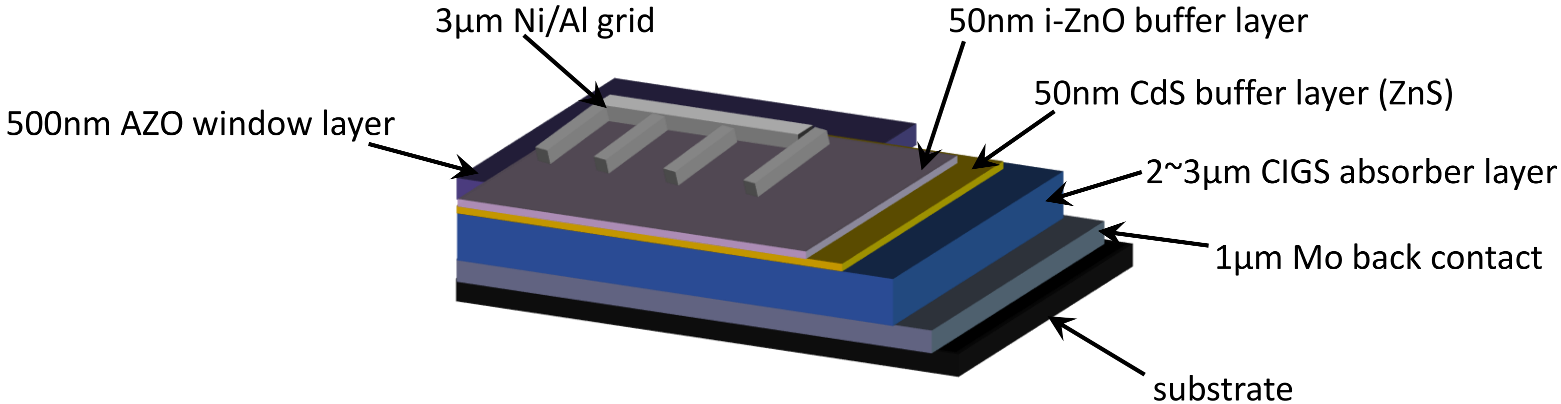


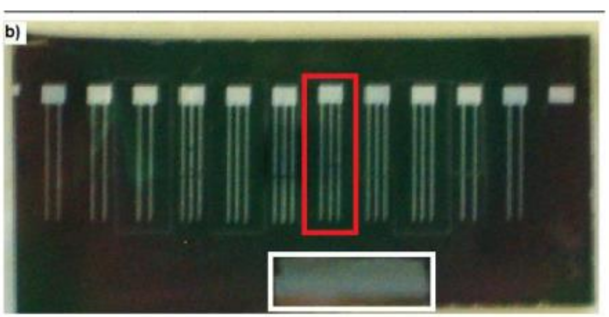
" transfer devices made by graphite stripes"

M.Acciarri & S. Binetti et al. Solar Energy , 175, 16-24 (2018)
S.Binetti et al Semicond. Sci . Technol. 30 (2015) 105006
J. Parravicini, et al. Applied Spectroscopy 71(6), 1334-1339 (2017)
J. Parravicini et al. Applied Optics, 57 (8), 1849 (2018)

Basic steps of CIGS solar cell process @ MIB-SOLAR

- Deposition time is 30 min (CIGS layer ≈2 µm)
- Deposition Process T = 550 °C (or 450 °C)
- Substrates: maximum size 20 cm x 120 cm in a roll-to-roll configuration
- R&D line that gets the cell and their characterization within less 24 h from deposition

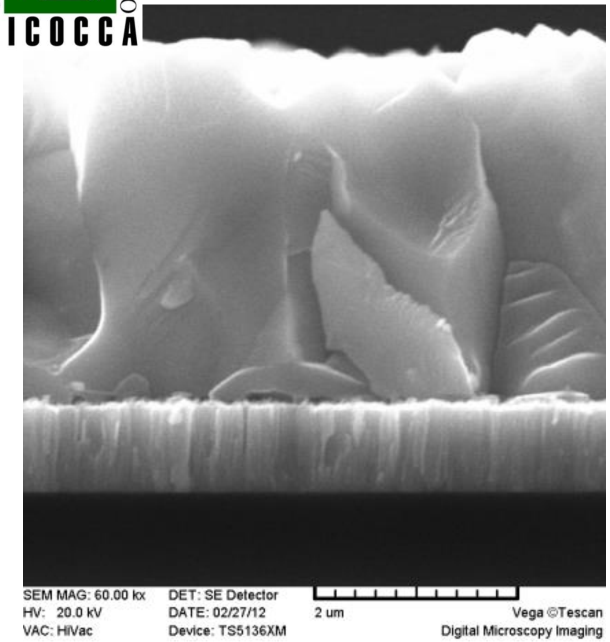




We define the cell size by mechanical scribing cell area equals 0.50 cm^2

CIGS Best results

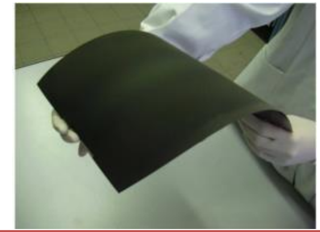
Without antireflection coating



Glass **T= 550 °C**

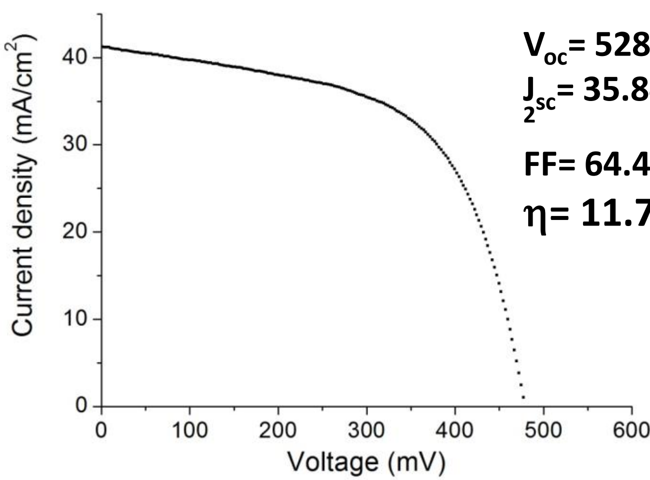
η [%]:	15 %
Voc [mV]:	581.7
FF [%]	72
Jsc [mA/cm^2]:	34.52
Area [cm^2]:	0.48

flexible steel foil (120 μm)



η [%]:	13.6
Voc [mV]:	540.6
FF [%]	70.65
Jsc [mA/cm^2]:	31.18
Area [cm^2]:	0.48

Polyimide **T =450°C**



V_{oc}= 528 mV
J_{sc}= 35.84 mA cm^{-2}
FF= 64.4 %
η= 11.7 %

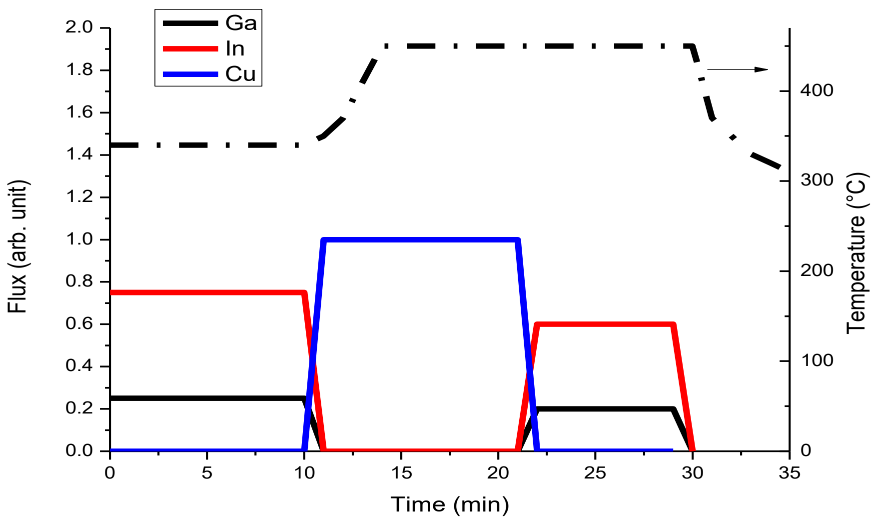
Flexible Thin glass (125 μm)

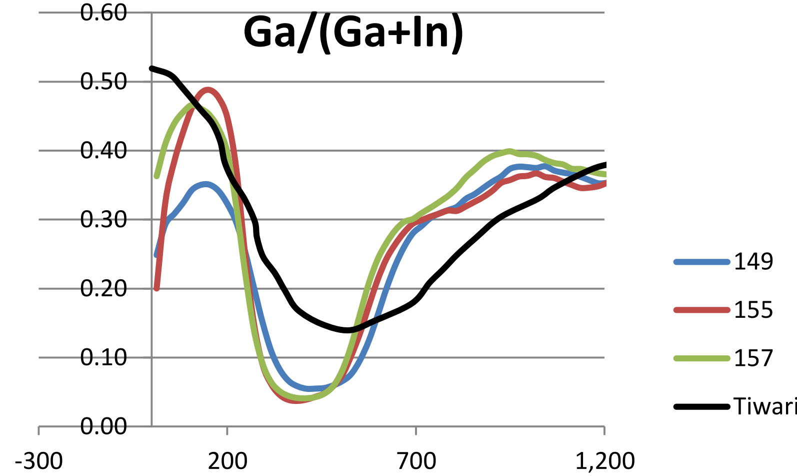
V_{oc}= 491 mV
J_{sc}= 38 mA cm^{-2}
FF= 67 %
η= 12.5 %

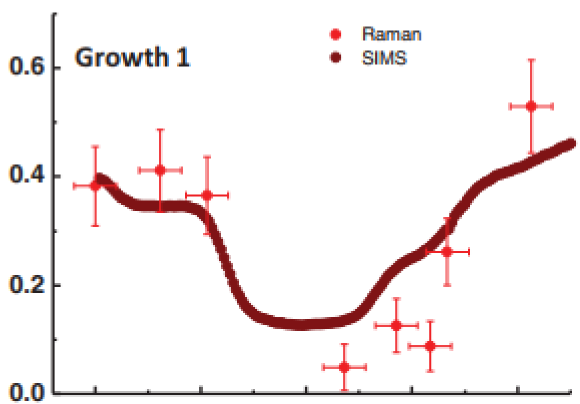
$CuGaS_2$

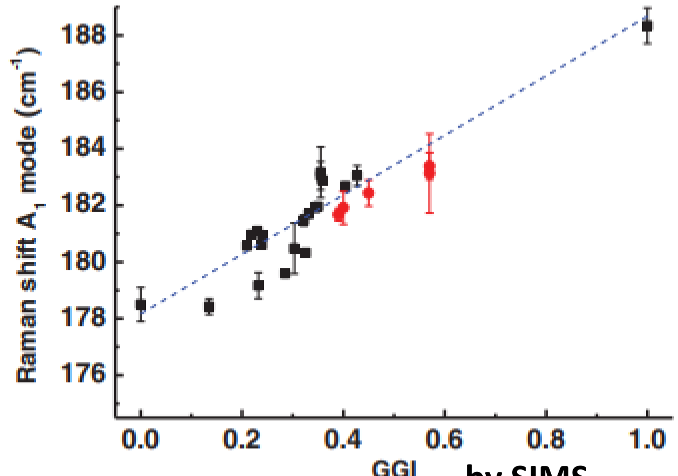
Eg= 2.4 eV
for tandem solar cells

A suitable [Ga]/([Ga]+[In]) (GGI) in-depth profile has proved to play a key role in the performance of cells.









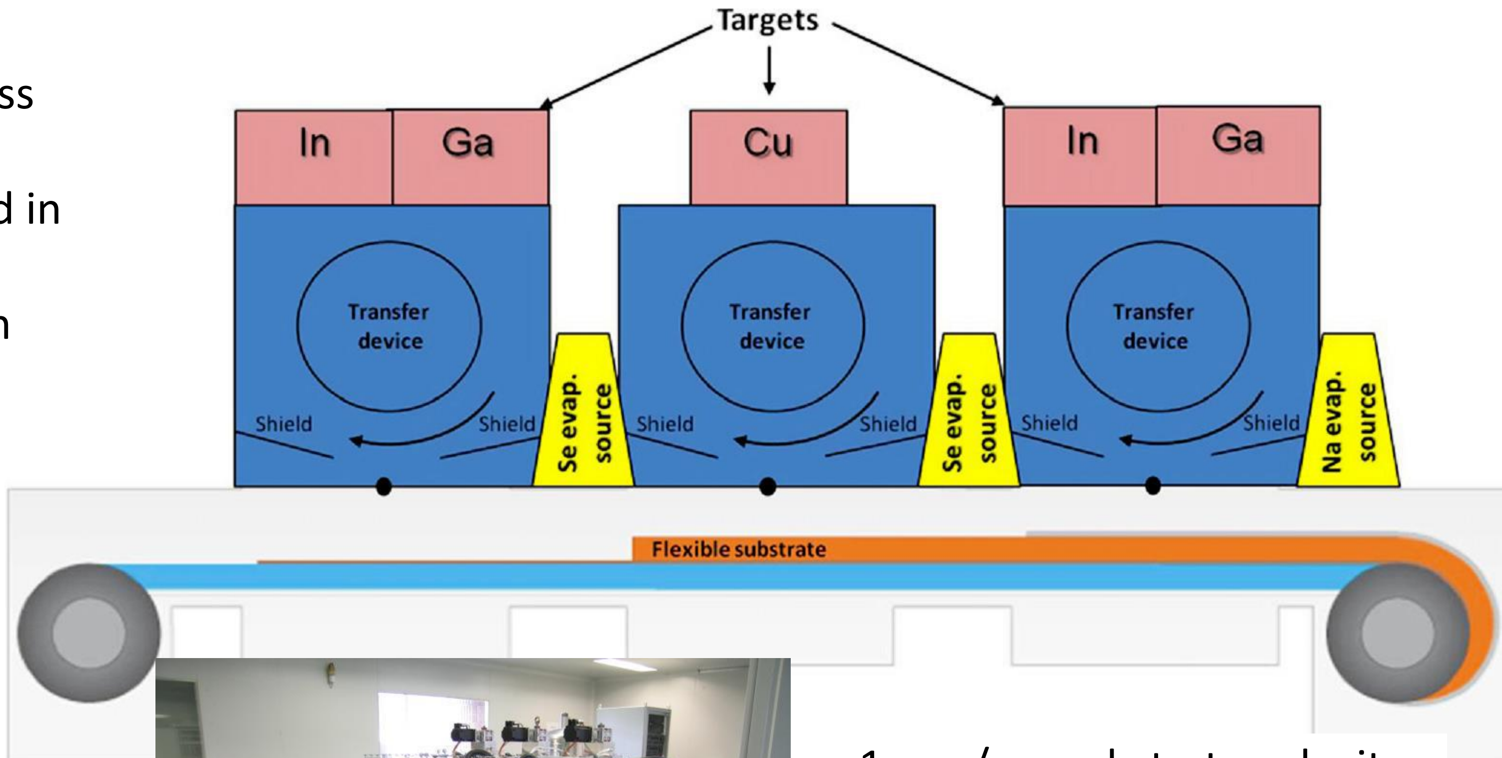
by SIMS

A new method based on repeated bromine etching of CIGS thin film and the measure of the A1 mode Raman shifts

Applied Spectroscopy 71(6), 1334-1339 (2017)

CIGS deposition system in production line

This process has been transferred in a 1 MW production line



1 mm/sec substrate velocity

http://sunplugged.at/

Critical Metals in Inorganic thin film PV Technologies

Abundance in Earth's Crust of the elements

Cu 0.0068 %
Zn 0.0078
Sn 0.00022 %
Ga= 0.0019%
Se= 5x 10^{-6}%
In = 0.00016%

Ga = 19 ppm
In= 0.25 ppm
Se = 0.05 ppm

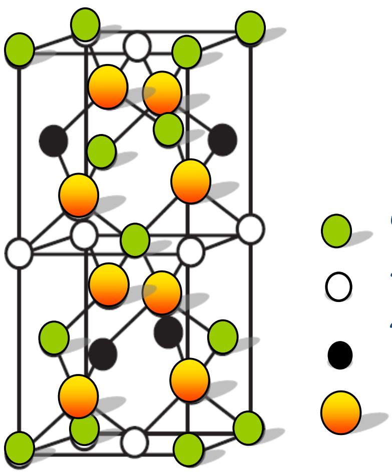
A.Le Donne, V. Trifiletti & S. Binetti "New Earth-Abundant Thin Film Solar Cells Based on Chalcogenides" Frontier in Chemistry 2019
doi: 10.3389/fchem.2019.00297

✓The current indium extraction rate permit to estimate a global CIGS solar module production less than 100 GWp
✓Due to the adverse effects on the environment and human health, the supply and use of cadmium is restricted in Europe under the REACH regulation
✓High price

To raise the competitiveness of thin films based modules, rare and toxic elements should be avoided in all layers of the solar devices.

Strong constraints impose to investigate new materials

Kesterite: Cu_2ZnSnS_4



- Kesterite structure
- (CZTS) Enviromentally friendly , low cost
- Intrinsic p-type conductivity (Cu_{Zn} antisite – V_{Cu})
- E_g can be tuned between 1.45 and 1.65 eV (DIRECT) or 0.95-1.05eV
- High absorption coefficient (> 10^4 cm^{-1})
- *Efficiency record* η_{record}= 11% * (CZTS) - 12.6% (CZTSSe)

*C.Yan et al. Nature Energy 2019, 3- 764

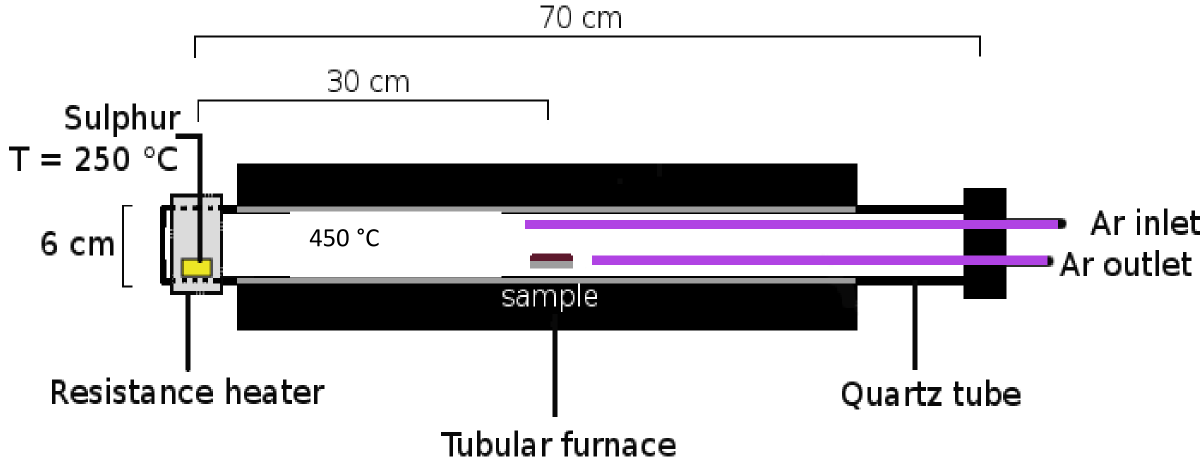
Cu_2ZnSnS_4 by sputtering

1 . Metal Precursos

-sputtering RF from Cu, Zn, Sn (5N) target on 5x2 cm^2 Mo coated SLG

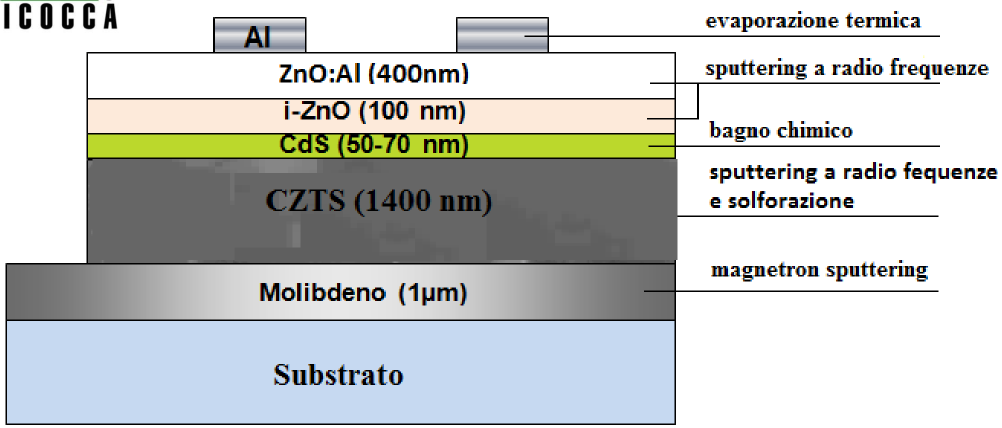
2 . Sulphurization process

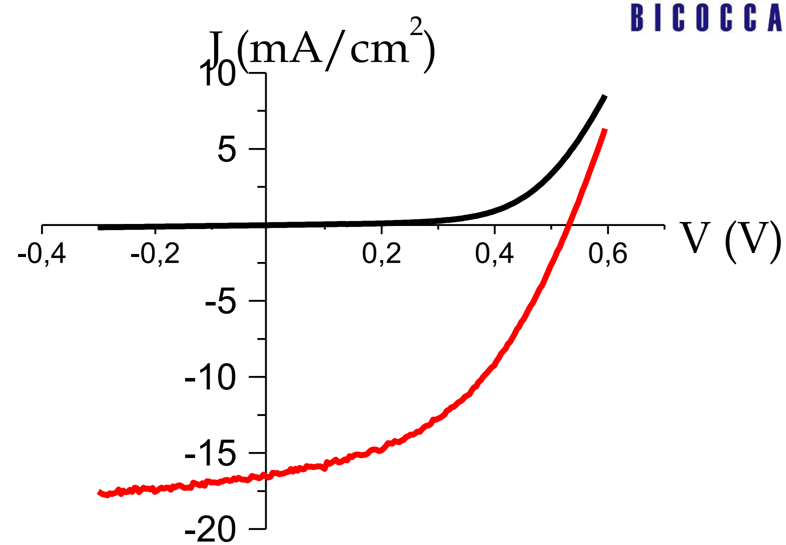
0.5 – 0.2 g of S in graphite crucible@250 °C in Ar flow = 30-40 cm^3/min - T= 550 °C for 60’



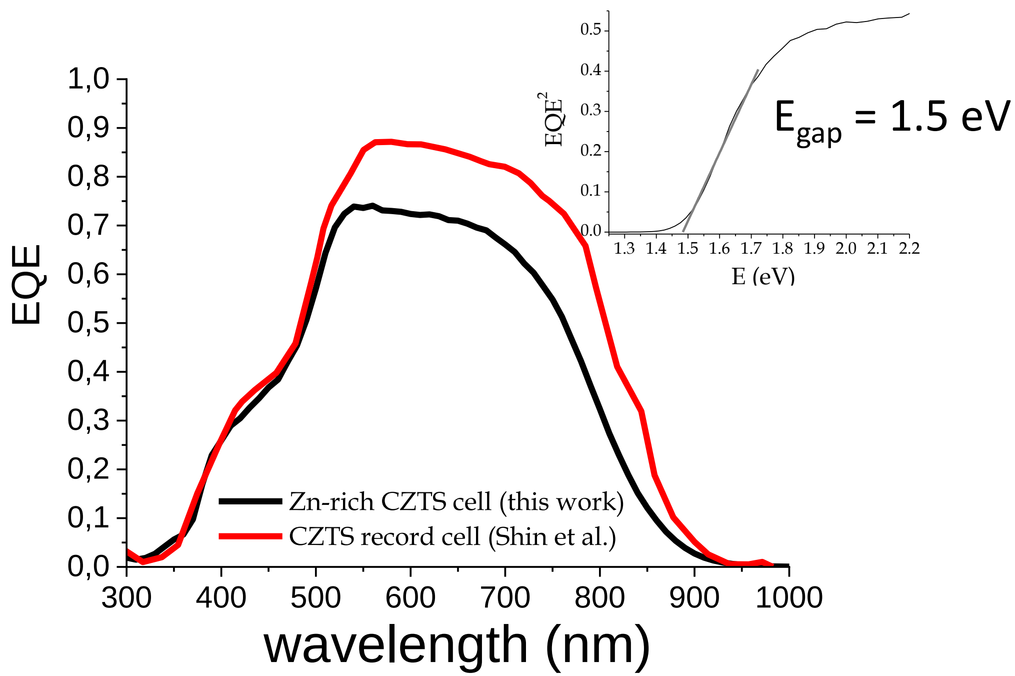
S. Marchionna, P. Garattini, A. Le Donne, M. Acciarri, S. Tombolato & S. Binetti Thin Solid Films **542**, 114 (2013)
A. Le Donne S. Marchionna, P. Garattini, R.A. Mereu, M. Acciarri & S. Binetti International J.of Photonergy (2015)

CZTS by sputtering results





Active area = 0.15 cm^2

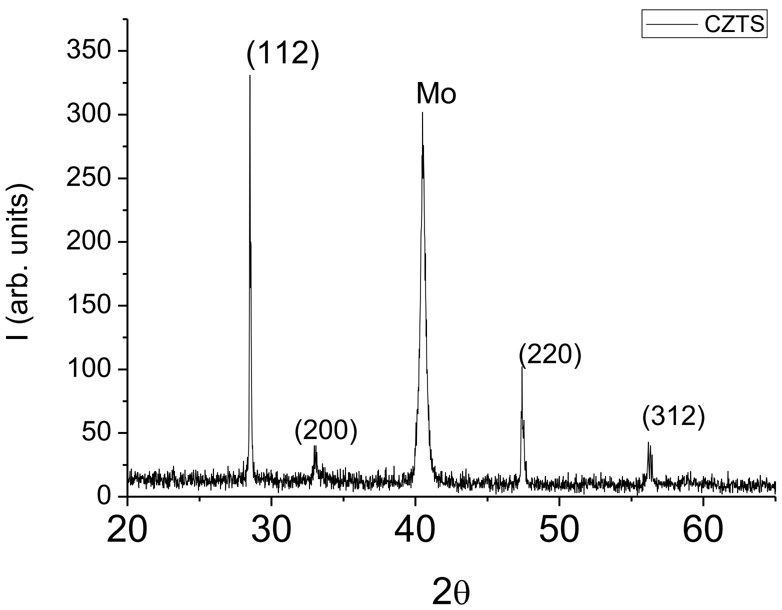


η [%]:	3,95		Voc (mV)	531
FF [%]	44,8		Jsc (mA/cm^2)	16,6

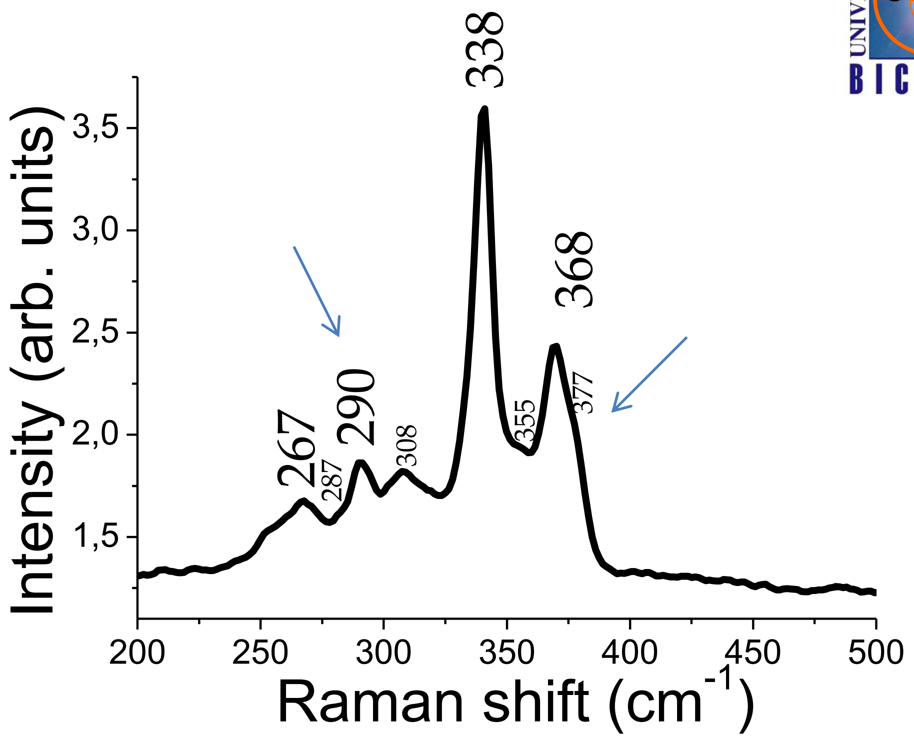
S. Marchionna, et al. & S. Binetti Thin Solid Films **542**, 114 (2013)

CZTS sputtering samples: Material Properties

Cu/Zn+Sn = 0.5
Zn/Sn = 2.3



Kesterite Structure

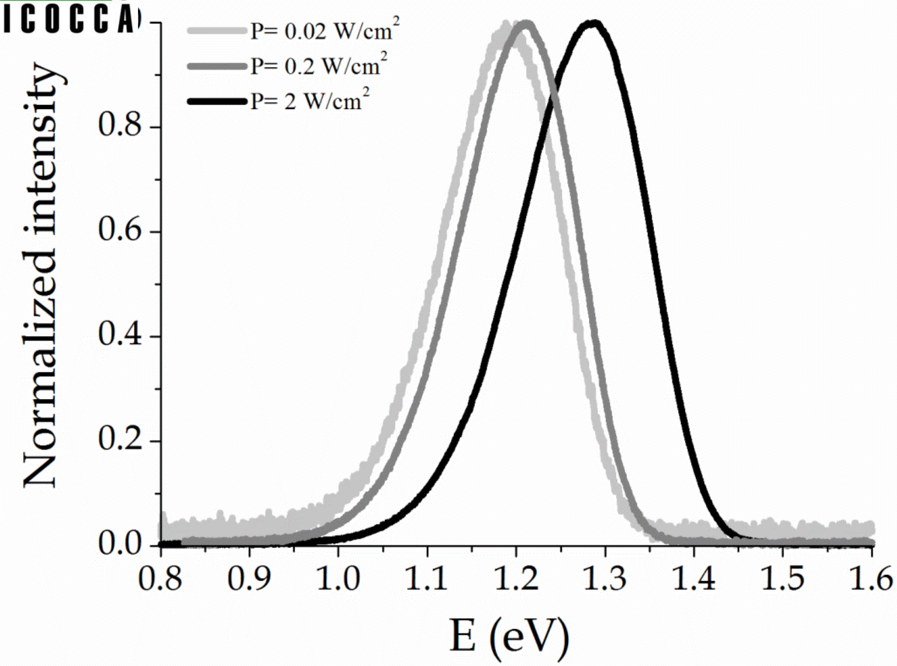


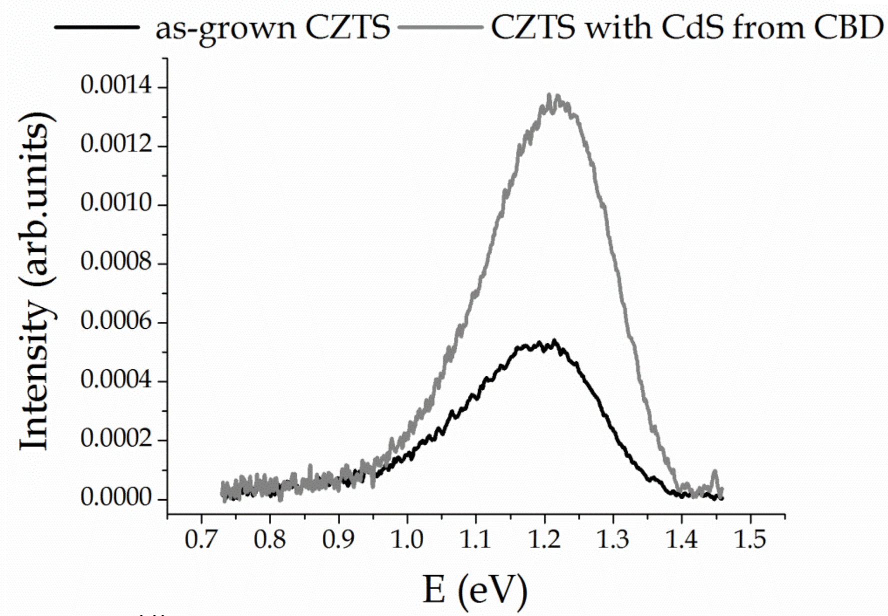
EDX :
The mean atomic concentration of Cu, Zn, Sn and S resulted 15%, 16%, 10% and 47%,

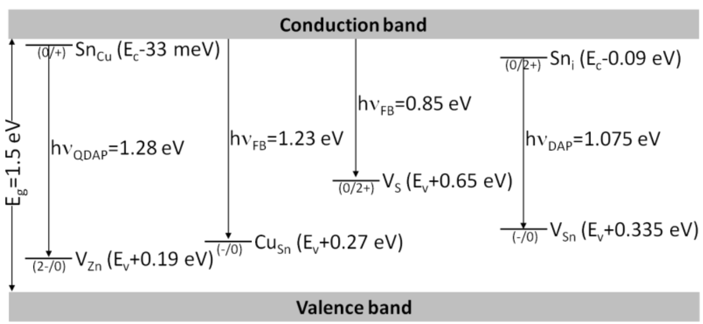
Along with the CZTS characteristic modes at 267, 287, 338 and 368 cm^{-1}, the Raman spectrum shows additional contributions at 290, 355 and 377 cm^{-1}, typical of cubic CTS

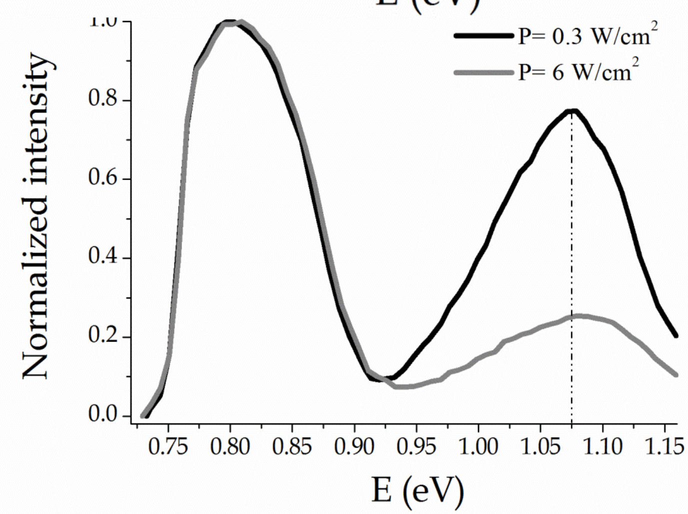
Eventually ZnS spurious phases were removed by etching in HCl (aqueous solution 5% at 75 °C for 300 sec).

CZTS defect identification by PL









A. Le Donne, S. Marchionna, P. Garattini, R.A. Mereu, M. Acciarri and S. Binetti " J. of Photonergy Volume 2015, Article ID 583058

High quality CZTS thin films by wet process

<u>Aim</u>: Develop a simple , cheap , no toxic process based on the sol-gel technique

Molecular inks :

CZTSsol was prepared by dissolving in DMSO:

- $Cu(CH_3COO)_2 \cdot H_2O$;
- $SnCl_2 \cdot 2H_2O$;
- $Zn(CH_3COO)_2 \cdot 2H_2O$.

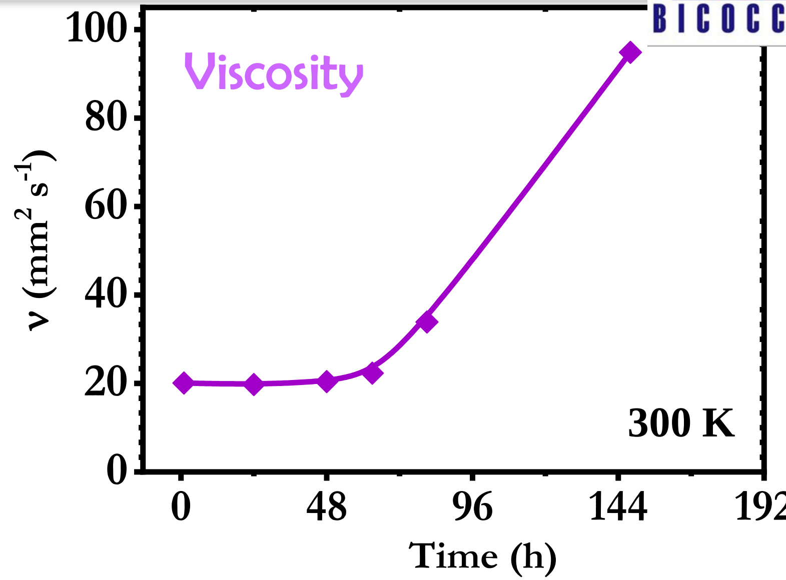
After complete dissolution, thiourea was added.

We investigated the composition and stability of the molecular ink

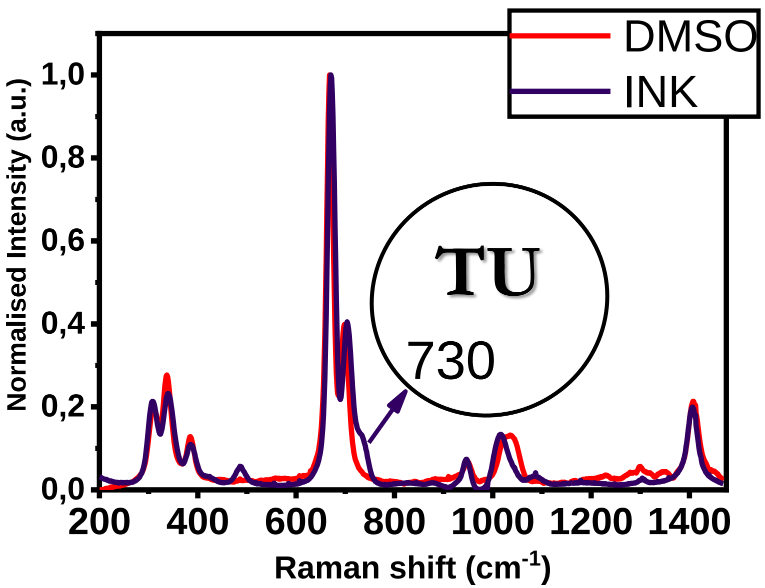
V. Trifiletti et al., Chemistry Select 2019, 4, (17), 4905-4912.

Sol-gel evolution

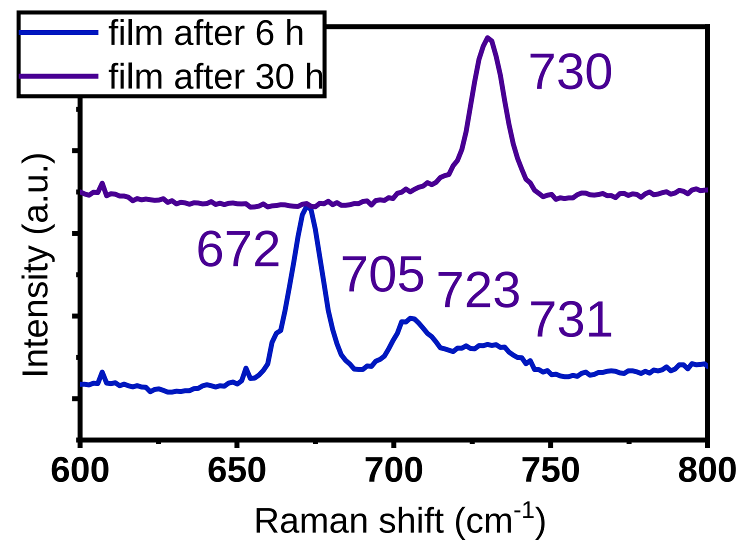
Ink composition :
$Cu(CH_3COO)\cdot H_2O$
$Zn(CH_3COO)\cdot 2H_2O$
$SnCl_2\cdot 2H_2O$
in (**DMSO** and **TU**)



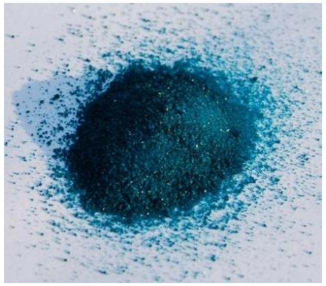
V. Trifiletti et al., Chemistry Select 2019, 4, (17), 4905



The Sol-gel viscosity increases due to polycondensation process, until the ink evolves to gel



After drying in air the DMSO signal disappears, and after 30 hours the thiourea signal splits in bands that are assigned to the metals coordinate by TU.


$Cu(CH_3COO)_2 \cdot H_2O$

0.8 mmol


$Zn(CH_3COO)_2 \cdot 2H_2O$

0.5 mmol


$SnCl_2 \cdot 2H_2O$

0.5 mmol


Thiourea

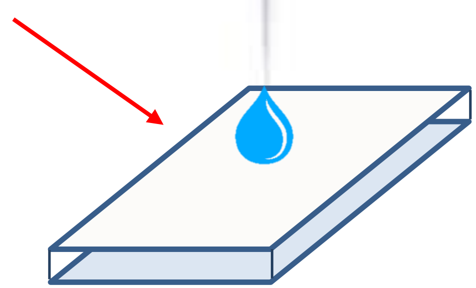
9.0 mmol

Solvent:
DMSO 3.0 mL

Thin films were fabricated by
1) a direct drop-casting of the solution
2) Gelation in 30' at RT after droplet deposition

loading
1st Layer: 4 μL/cm^2
2nd Layer: 6 μL /cm^2

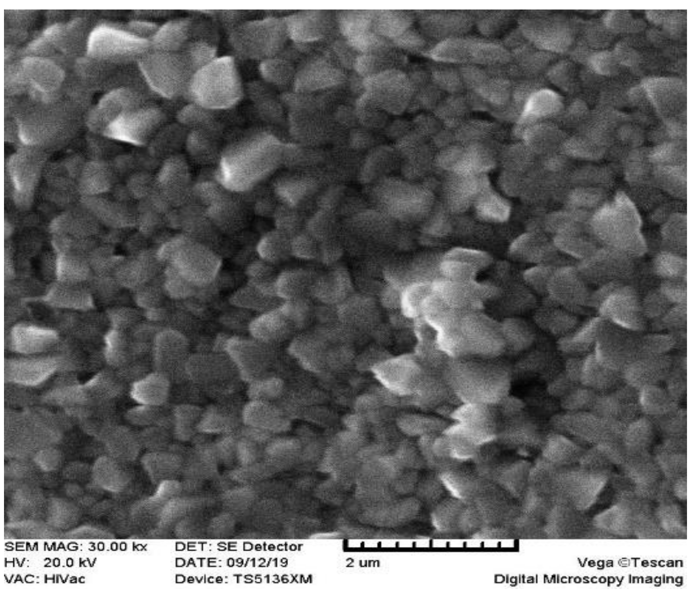
3) 1st and 2nd Layer:
Oven annealing in Argon @ 550 °C

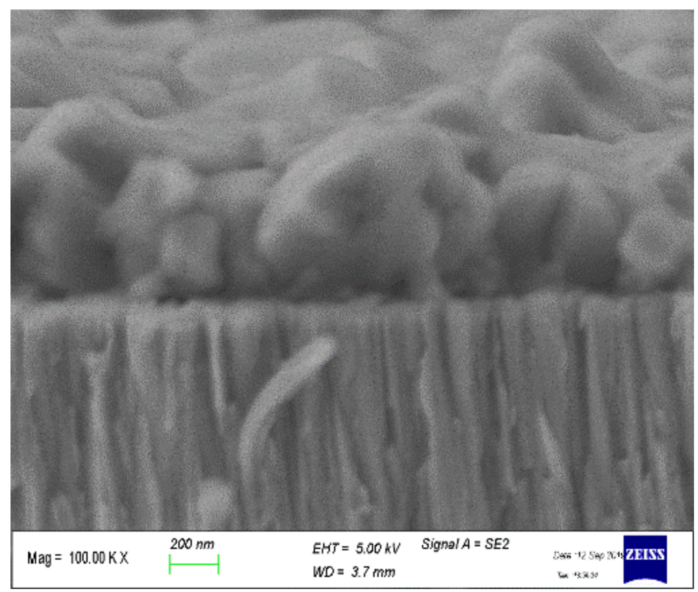


final thickness:
1.2 -1.5 μm

Optimization of the solution/film

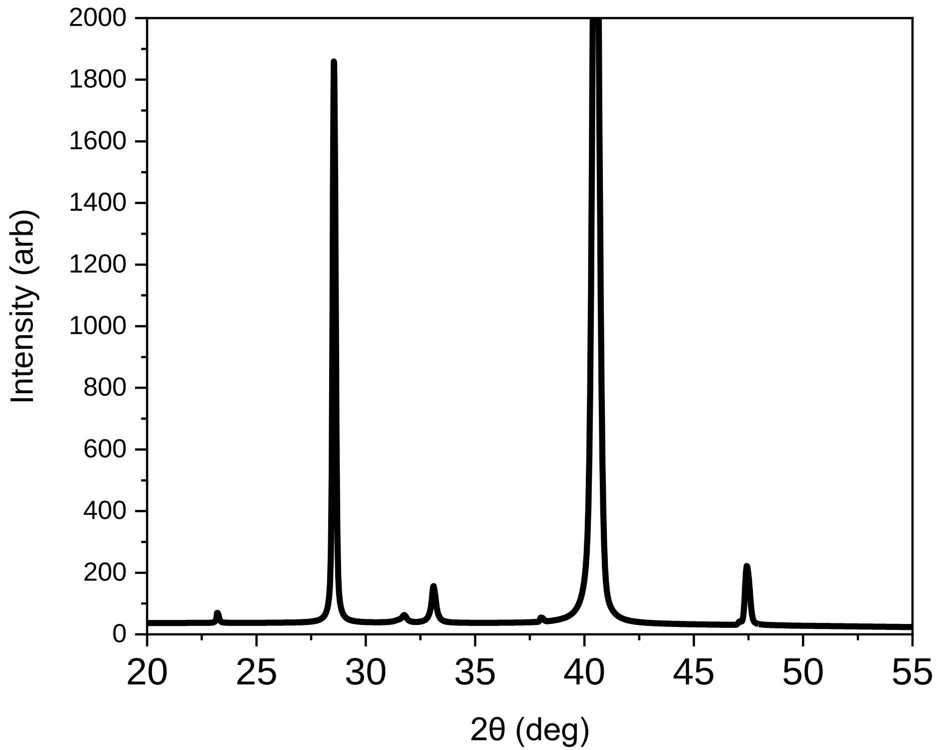
Entry#	Cu/(Sn+Zn)	Zn/Sn	Thiourea [conc.]
1	1.00	1	3.7 M
2	0.91	1	3.7 M
3	0.86	1	3.0 M
4	0.83	1	3.0 M
5	0.80	1	3.0 M
6	0.80	1.1	3.0 M
7	0.80	1.2	3.0 M
8	0.80	1.2	2.3 M



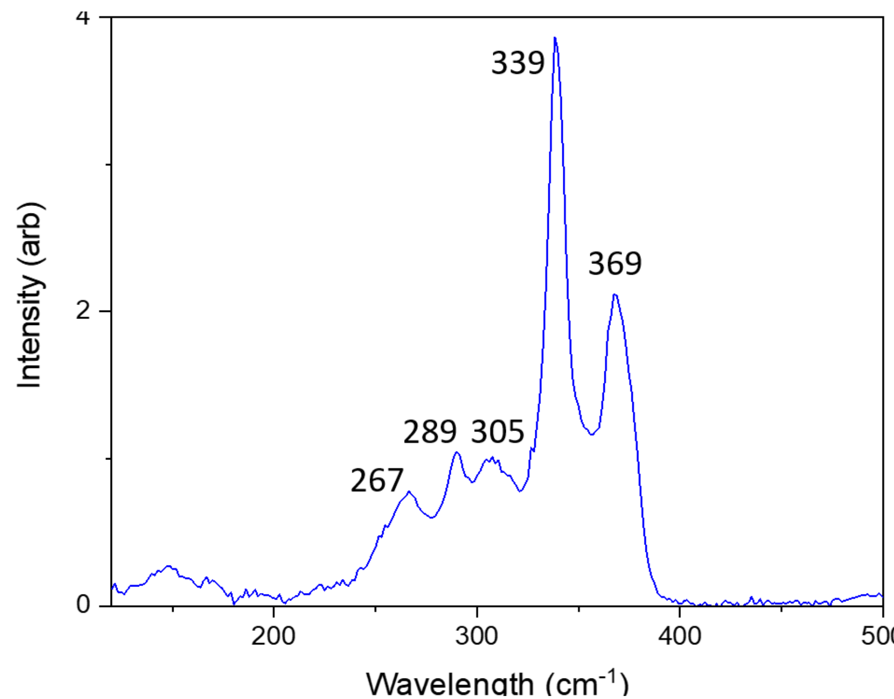


CZTS drop casting samples: material properties

XRD



Raman Spectra

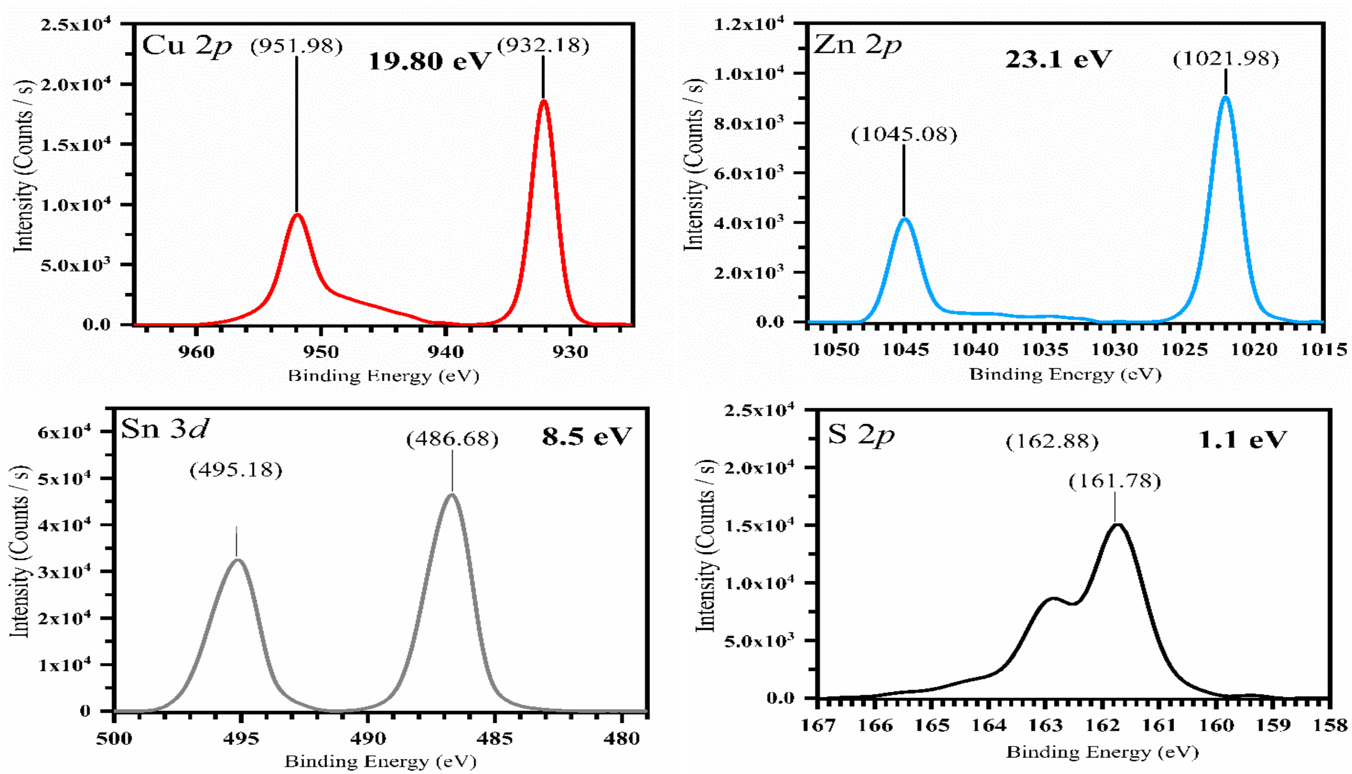


2θ = 16.5, 18.4, 23.3, 28.7, 33.2, 47.5

Unpublished results

XPS analysis on CZTS film

From Ms. Sally Luong, Dr Vanira Trifiletti and Dr Oliver Fenwick
School of Engineering and Materials Science ,Queen Mary University of London



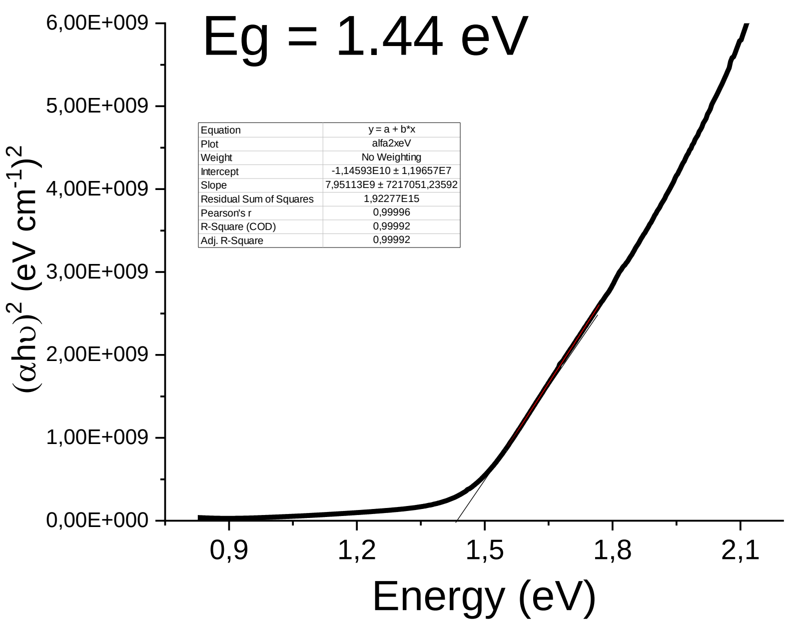
Ion Beam Etch:
30 sec x 3 times
(30 nm each time)
Energy 8000 eV
Raster size 1 mm
Cluster size 1000

Cu, Zn, Sn, and S oxidation states: Cu (I), Zn (II), Sn (IV) and S (II)

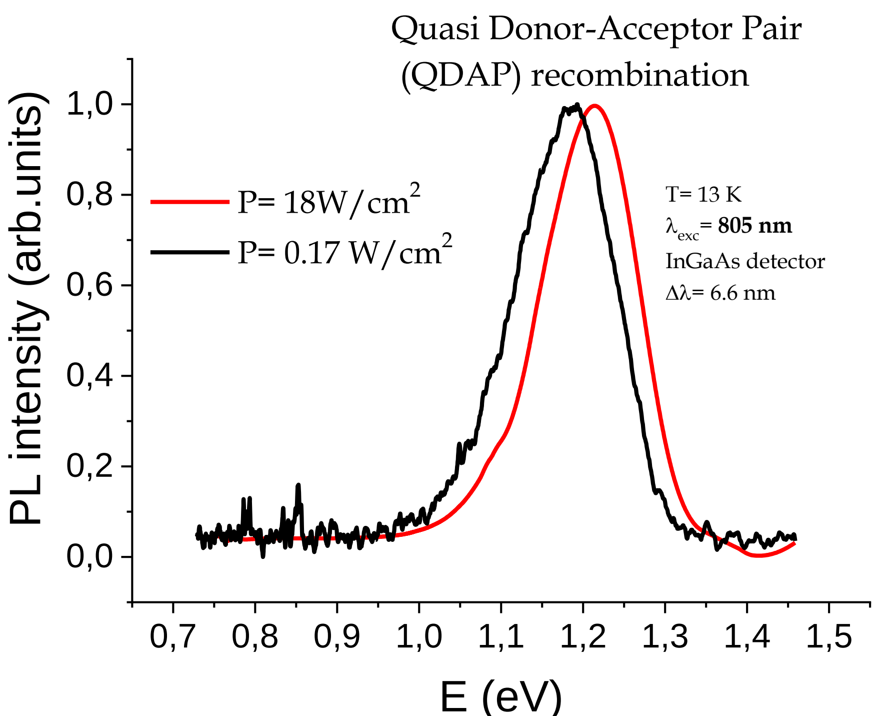
Sample #2

Unpublished results

Band gap and PL

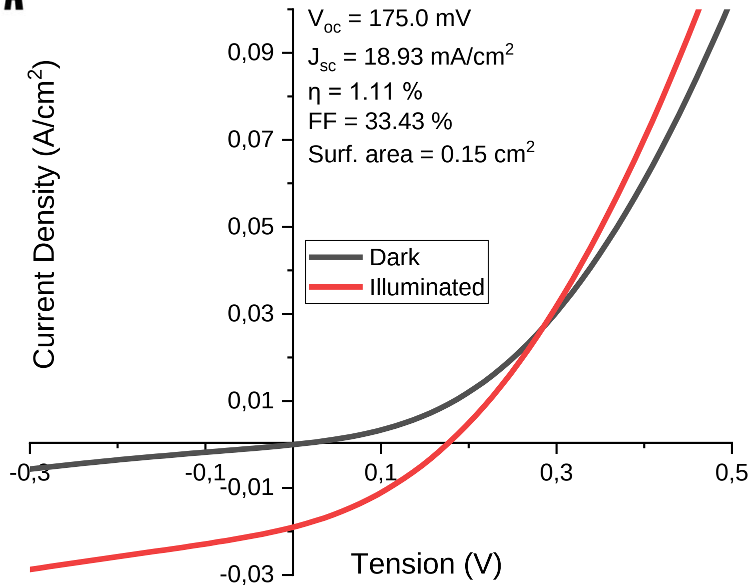


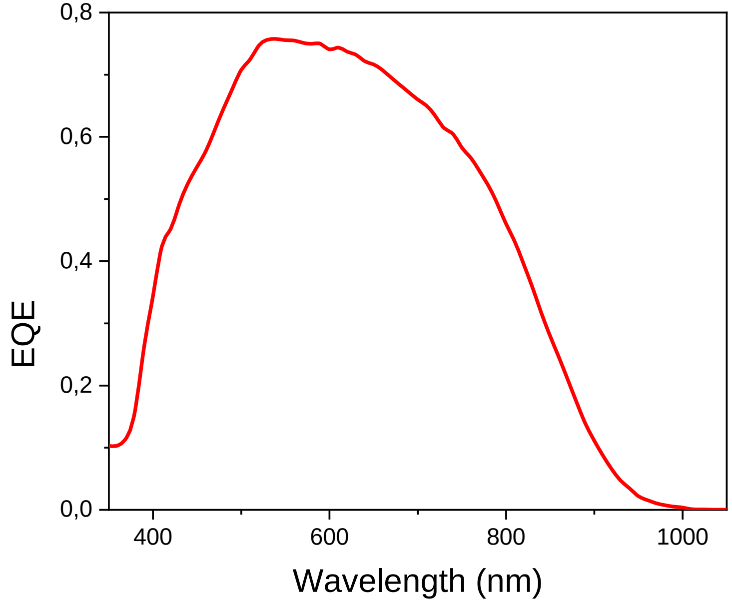
Equation	y = a + b*x
Plot	alfa2xeV
Weight	No Weighting
Intercept	-1,14593E10 ± 1,19657E7
Slope	7,95113E9 ± 7217051,23592
Residual Sum of Squares	1,92277E15
Pearson's r	0,99996
R-Square (COD)	0,99992
Adj. R-Square	0,99992



Unpublished results

Device Performance





V_{oc} = 175.0 mV → **Modest V_{oc}**

J_{sc} = 18.93 mA/cm^2 → **Respectable J_{sc}**

η = 1.11 %

FF = 33.43 %

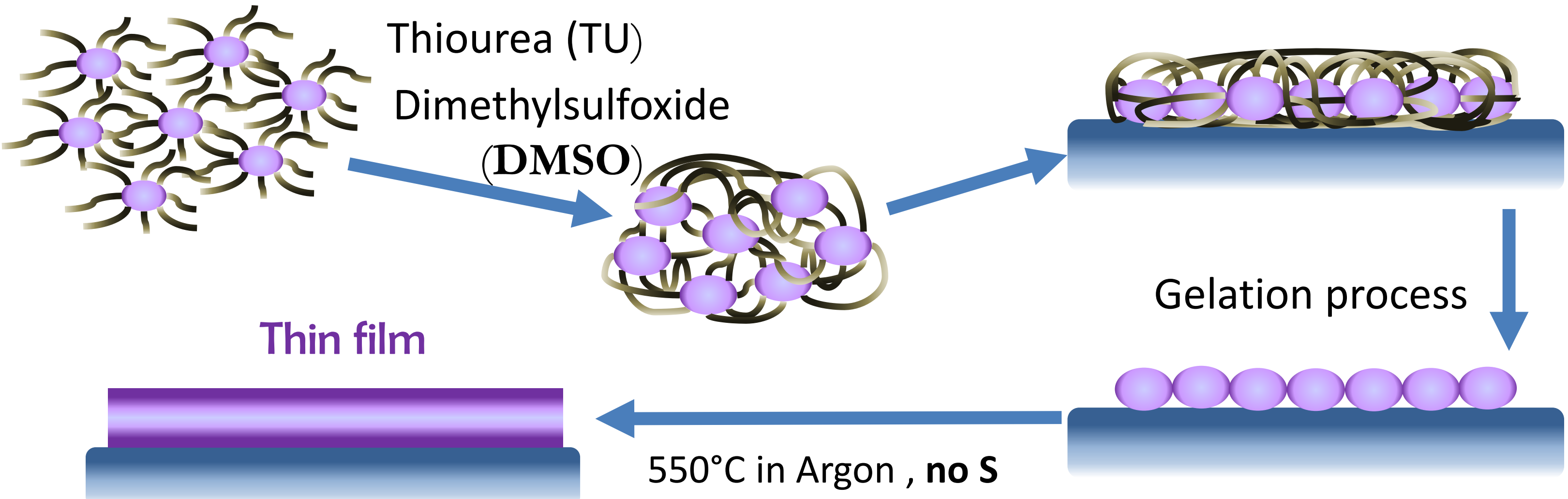
SCAPS software simulation indicates problems at the interface with the back contact

Unpublished results

Kesterite thin films by non toxic solution process

Several deposition methods

1 **Precursor Ink**



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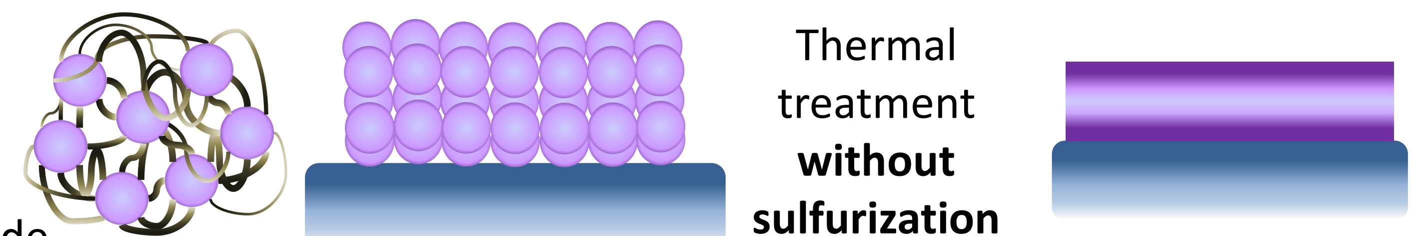
2 **Precursor-ink** → Spin Coating on substrates on **FTO or** Mo Glass) → Cu_2ZnSnS_4 Thin-film

Metal salts

Thiourea

Dimethylsulfoxide



3 **Precursor-ink** + a ink jet printer (in progress)

V. Trifiletti et al., Chemistry Select, 2019

Tuning the gap

UNIVERSITÀ DEGLI STUDI DI MILANO BICOCCA

$Cu_2Zn_{1-x}Fe_xSnS_4$

Molecular inks :

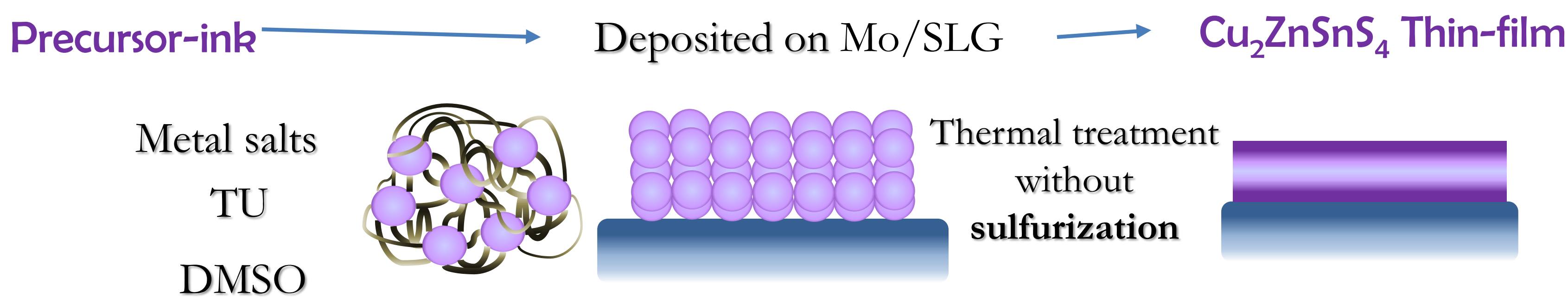
CZFTS sol was prepared by dissolving in DMSO:

- $Cu(CH_3COO)_2{\cdot}H_2O$;
- $SnCl_2{\cdot}2H_2O$;
- $Zn(CH_3COO)_2{\cdot}2H_2O$.
- $Fe(CH_3COO)_2$

After complete dissolution, thiourea was added.

Ink is spread on Mo SLG and HT @550 °C in S
Preliminary thin film results very promising

CZTS by wet process : summary



In the precursor-ink:

- ✓ TU acts as a monodentate ligand for the metal ions and DMSO solvates them;
- ✓ DMSO supports TU coordination.

Kesterite phase formation in the final film is supported by:

- ➢ the acetate groups, which bridge the different metal ions, creating a network, and favour the sol-gel formation;
- ➢ the homogeneous distribution of the components.

- ➢ Promising material quality and I_{sc}

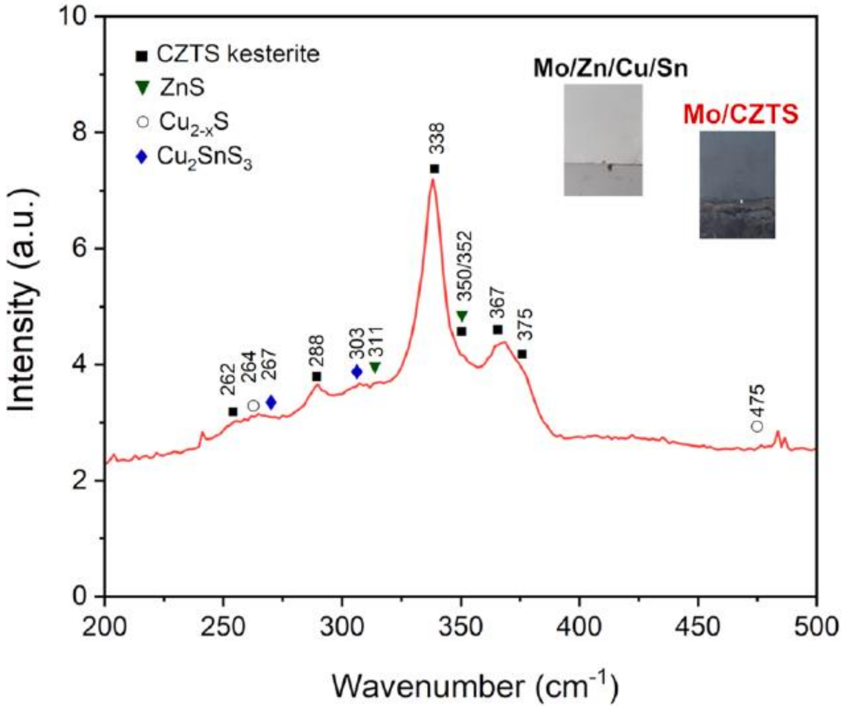
Open questions

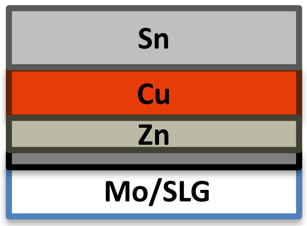
Low efficiency (problem with back contact (MoS_2 ?), no etching with KCN, intermediate passivation layer , alternative buffer layers…

CZTS by electrodeposition

is one of the most attractive fabrication routes: large area and low-cost process and easily scalable

stack elemental layers approach of CZT precursors + sulfurization





Advantages :

- Fast steps
- Control on stoichiometry (layer thickness)
- Scalable to large surfaces
- Constrained stacking order

- Lower quality than vacuum processes

non-aqueous plating solution:

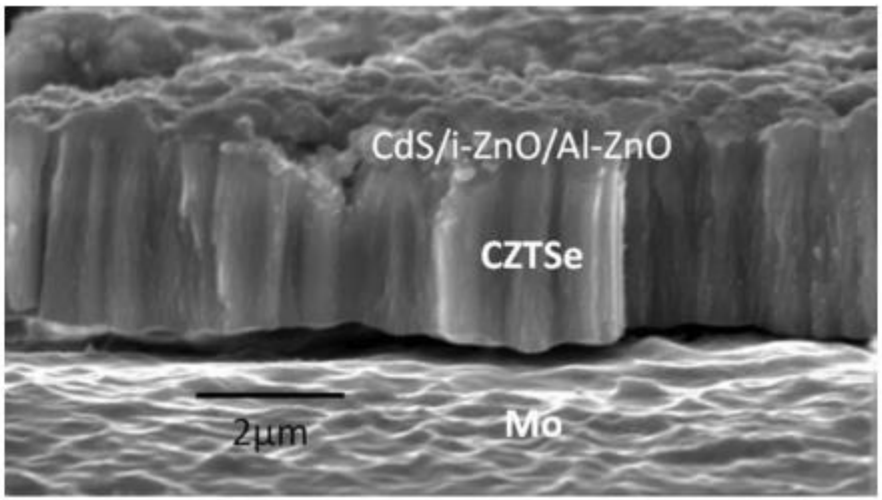
Anhydrous ethylene glycol ; copper acetate 0.05 M ; sodium acetate 1 M ; diethanolamine 0.8 M; dimethylamine borane complex 0.1 g/L

Zn/Sn =1.1 Cu/Zn+Sn = 0.85

G. Panzeri et al. Electrochemistry Communications 109 (2019)

CZTSe by electrodeposition

Co-electrodeposited Cu-Zn-Sn precursor + sulfurization or selenization on Mo flexible foil which acts both as a substrate for the electrodeposition process and as a back contact



0.1% with Jsc= 3.9 mA/cm2 ,
V_{oc}= 119 mV in our first attempt.

M.I.Khalil, et al ."*Co-electrodeposition of metallic precursors for the fabrication of CZTSe thin films solar cells on flexible Mo foil*" Journal of The Electrochemical Society, 164 (6) D302-D306 (2017)

ALTERNATIVES TO CZTS: $Cu_2M^{(II)}M^{(IV)}S_4$

with M(II) = Zn, Mn, Fe, Ni, and M(IV)= Si, Ge, Sn

Cu_2MnSnS_4

- A new alternative:
  - p-type semiconductor fully based on Earth-abundant and low-cost elements :
  - the abundance in the Earth's crust of Mn is two order of magnitude higher than that of Zn (1100 ppm vs 79 ppm)*,
  - is definitely cheaper (the amount of Zn produced in 2015 was 4'600'000 tons lower than that of Mn (13'400'000 Zn tons vs 18'000'000 Mn tons).
  - Lower Wp cost
  - Up to last year studied as Diluite Magnetic Semiconductor

*A. Le Donne, V. Trifiletti , & S.Binetti * Frontier in Chemistry 2019

Cu_2MnSnS_4

Vacuum approach: **Metal precursors evaporation followed by annealing in elemental sulfur vapors**

Metal Precursors:
4-sources EB evaporation system
+ Sulfurization

Standard stack structure	Double stack structure	Sandwich stack structure
		

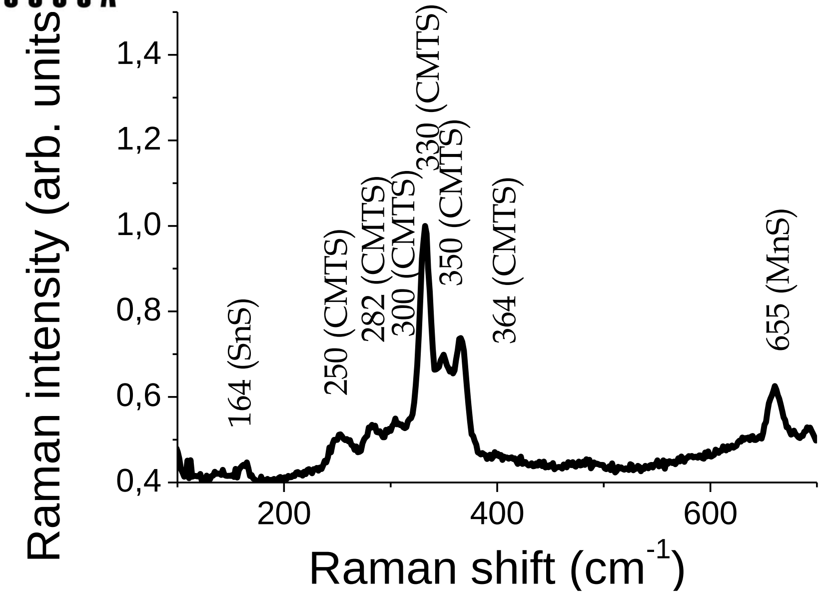
-Testing :
-the thickness and order of the metal precursors in the evaporated stack
-Annealing temperature : 500°C, 525°C, 555°C, 585°C, for 1 h (ramping rate:15°C/min)

- Pre-annealing to enhance metal intermixing(115°C for 1 h).

Substrates: soda lime glasses coated with sputtered Mo 1 µm

Deposition rate: [Sn] = **0.25** nm/s, [Cu] = **0.12** nm/s, [Mn] = **0.3** nm/s

Cu_2MnSnS_4 thin film: main properties



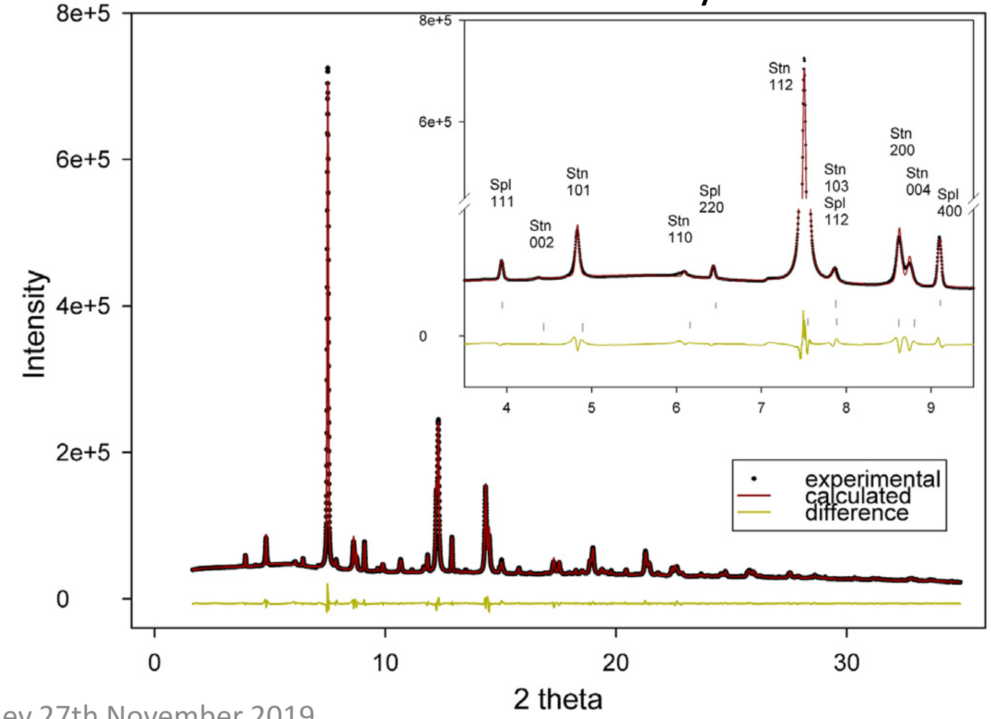
✓EDX and Raman analyses confirm that the **CMTS phase** was obtained

✓Lower content of insulating MnS secondary in the case of lower Mn layer thickness (i.e. 135 nm)

✓Stannite Structure

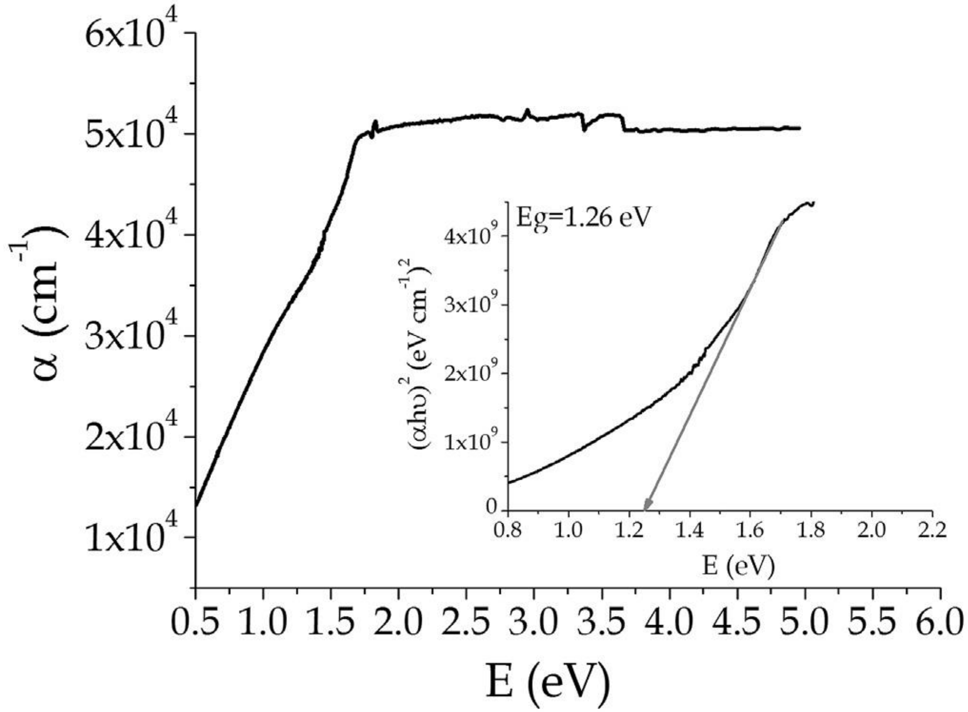
(+ sulfide compound with spinel structure)

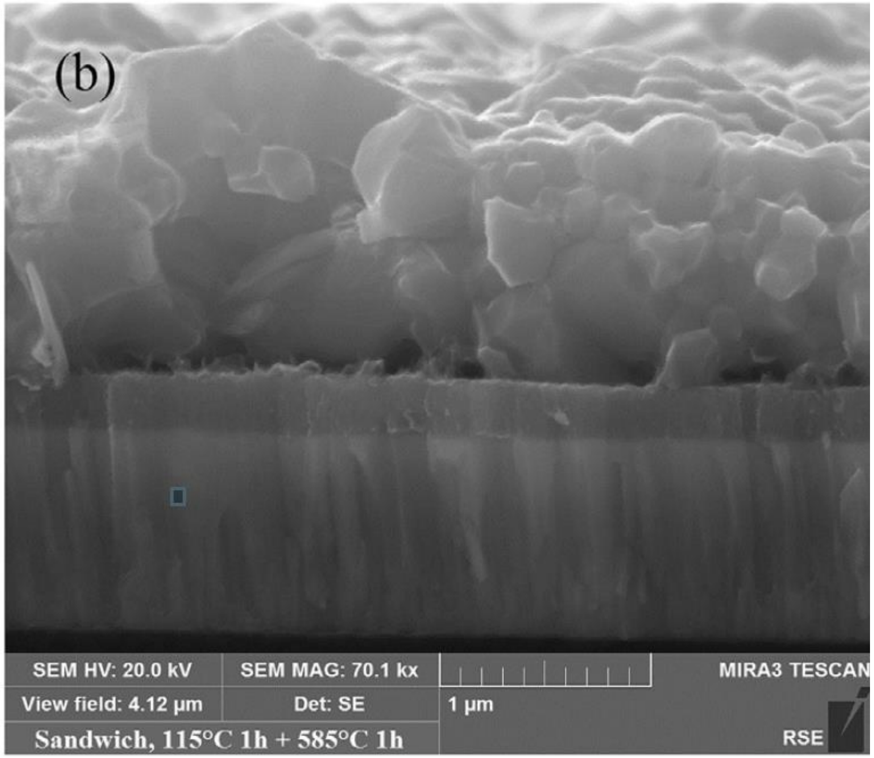
ID09A beamline at ESFR Synchroton



S. Marchionna et al . J.of Alloys and Compounds 693 (2017) 95

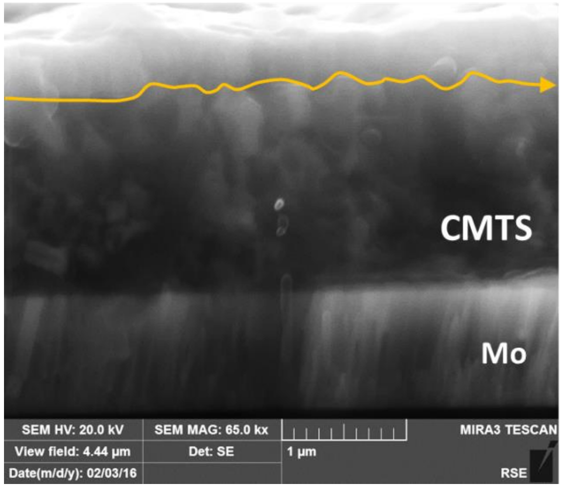
Cu_2MnSnS_4





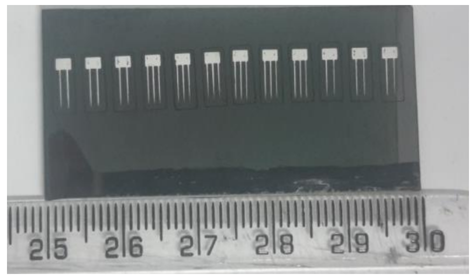
✓ high absorption coefficient (**$5x10^4$ cm^{-1}**) and direct band (**1.26 eV**) suitable for PV applications have been obtained

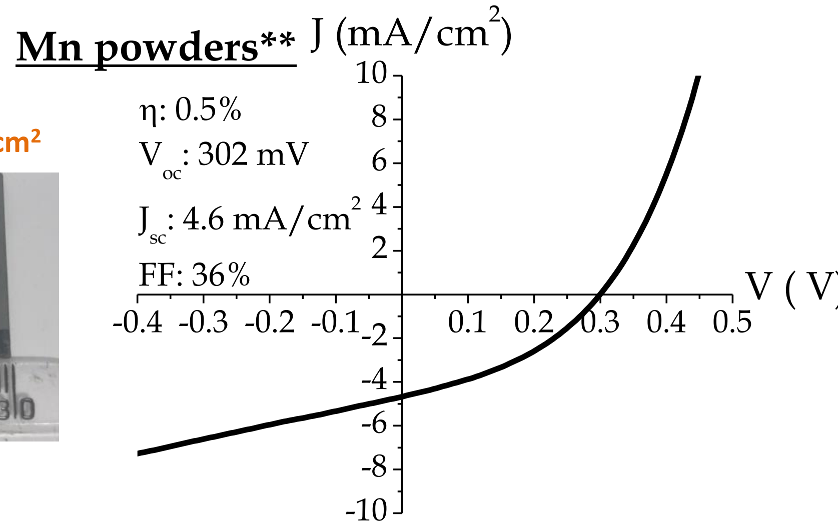
Cu_2MnSnS_4: solar cell prototypes

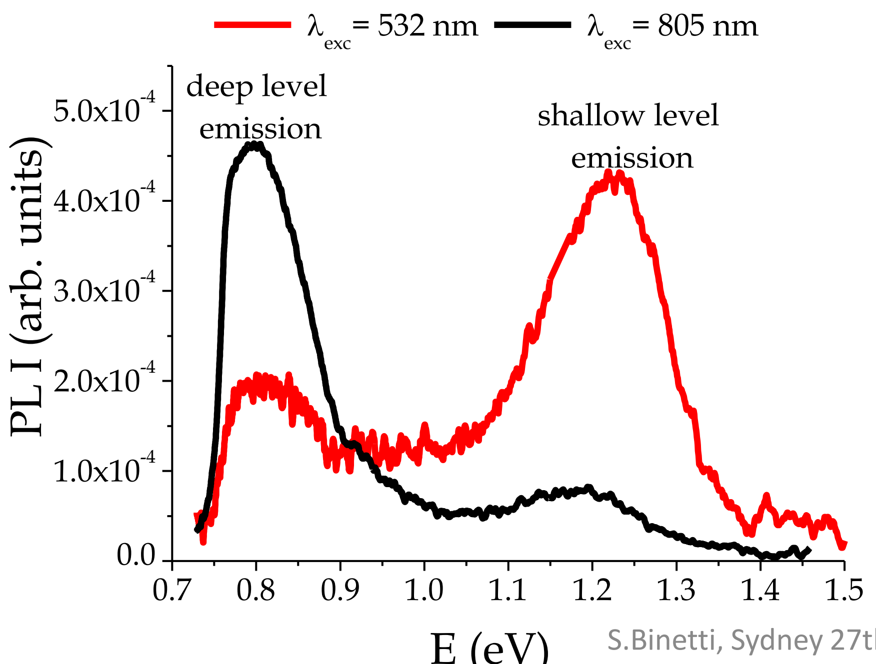


AZO (≈ 350 nm) via DC–pulsed sputtering
CdS (≈70nm) via CBD +
ZnO-i (≈80nm) via RD sputtering

CMTS solar cells area = 0.15 cm^2



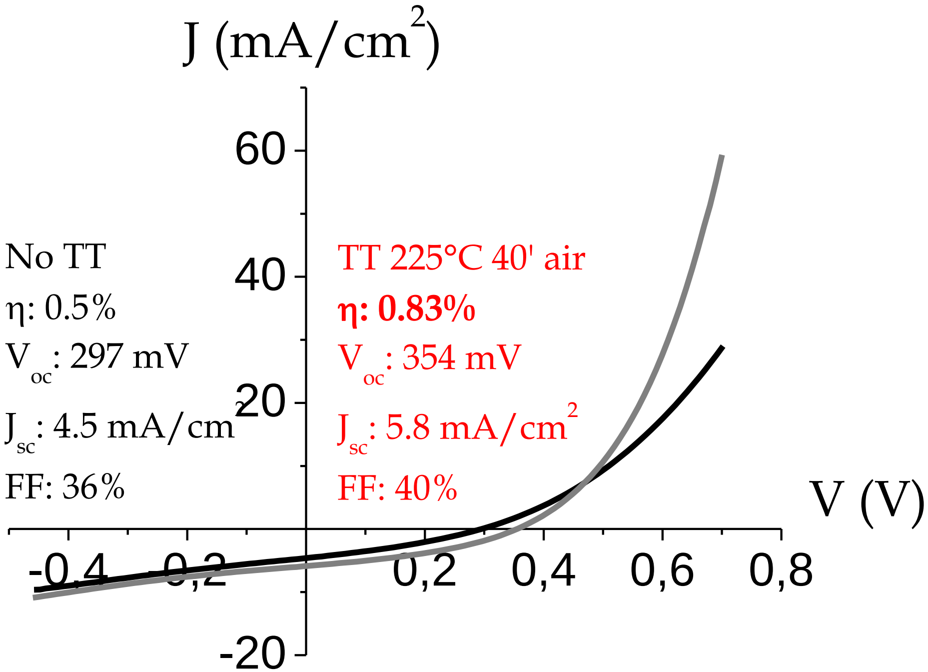


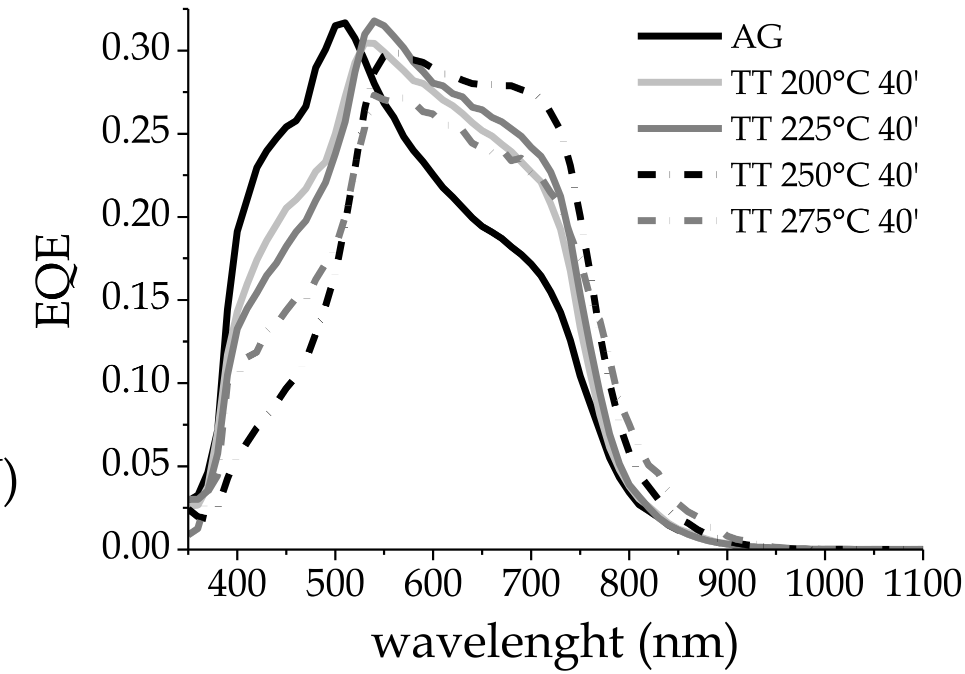


✓ Deep recombination center responsible for the emission at **0.8 eV** is associated to a **bulk defect**.

✓Secondary phases (sulfurization ramping rates to be reduced)

Effect of low temperature annealing on PV performance



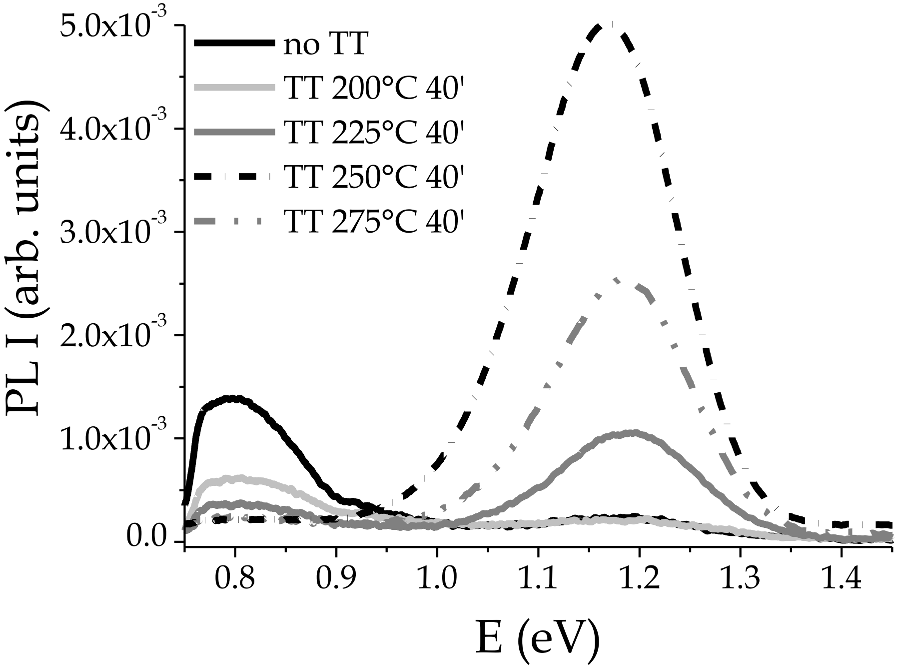


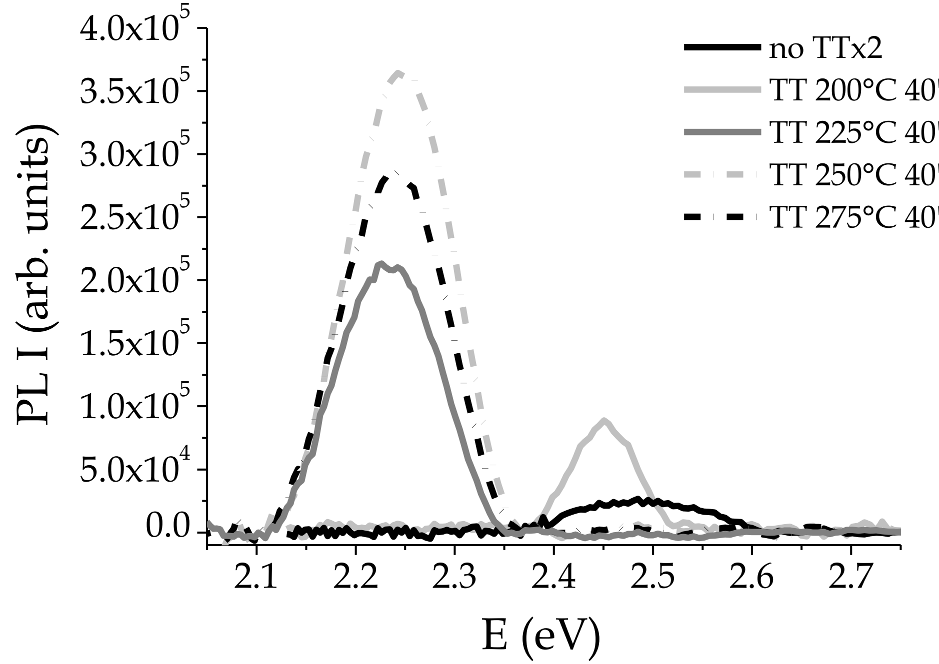
✓ annealing at 225°C allows for an improvement of all the device parameters, to 0.83% efficiency

EQE analyses which show a significant increase of the spectral response between 550 and 800 nm for all the tested temperatures, indicating
a reduction of recombination losses. But a gradual decrease of EQE in 350 -550 range

It is the present record as Chen et al. (2015) reported 0.49% maximum efficiency on CMTS layers prepared by direct liquid coating

Effect of low temperature annealing on bulk properties





- ✓ low-temperature annealing generally reduces the density of the deep bulk defect responsible for the emission at 0.8 eV, thus reducing recombination losses.
- ✓ before any annealing, CdS shows a very weak PL emission at about 2.5 eV, (nc-CdS) ; After 200 C annealing the PL signal increases and shifts to 2.45 eV indicating an improvement of CdS crystalline quality, and reducing the Eg value (i.e. 2.25 eV).

A. Le Donne, et al. Solar Energy 149 (2017) 125–131, 3283

Conclusion and Future works

- ✓ We have developed an innovative way to achieve high-quality kesterite thin-films suitable for PV
- ✓ CMTS: a new earth abundant material have been tested as PV absorber
- ✓ CZTS by electrochemical approach is under investigation

To be done :

- ➢ Reducing harmful defects in CZTS and CMTS
- ➢ Testing alternative Buffer layer to replace CdS by ALD (i.e. $Zn_{1-x}Sn_xO_y$ or Zn(O,Se)
- ➢ CMTS and CFTS by ink approach on flexible substrate

Final aim : USE a low cost solution process to get a full inorganic earth abundant based multijunction solar cells

Thank you for your attention !

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MIB-SOLAR

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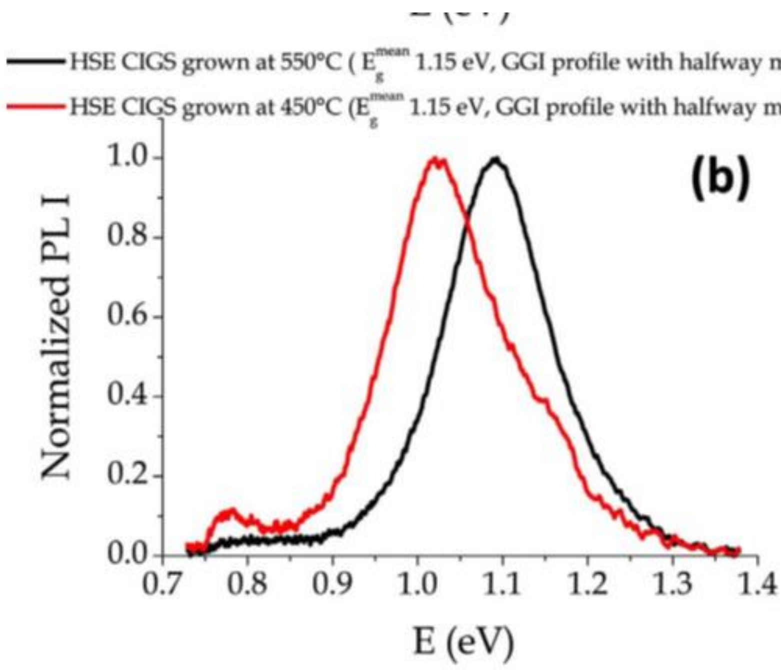
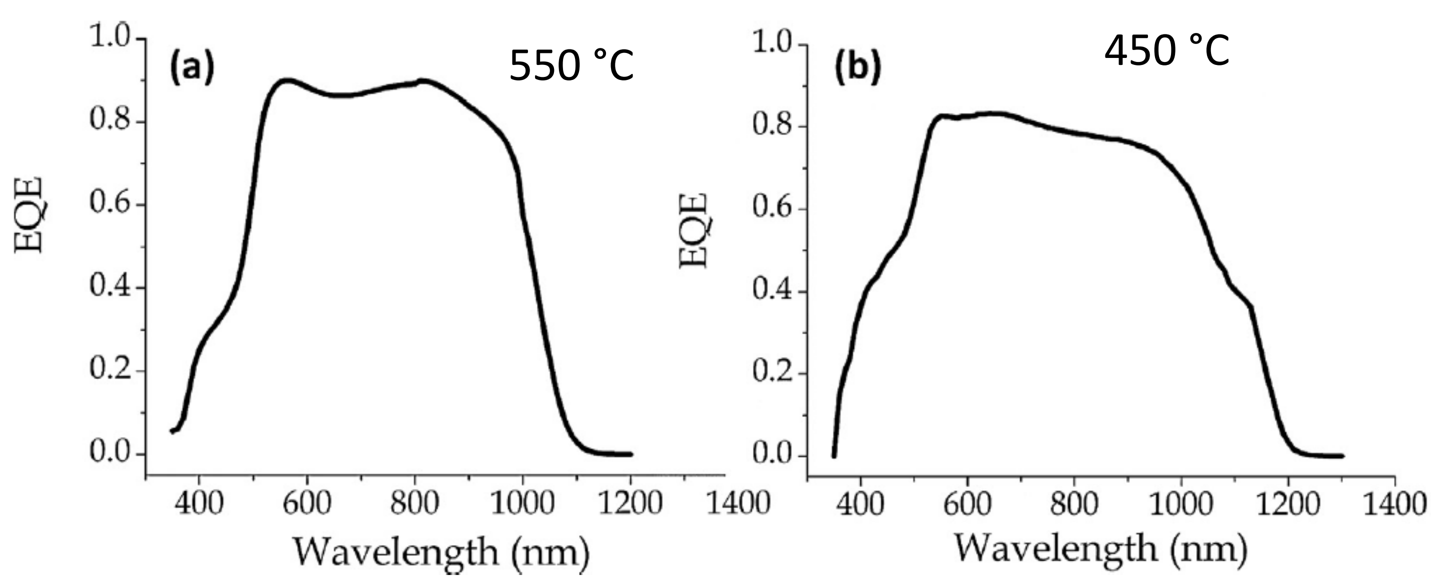
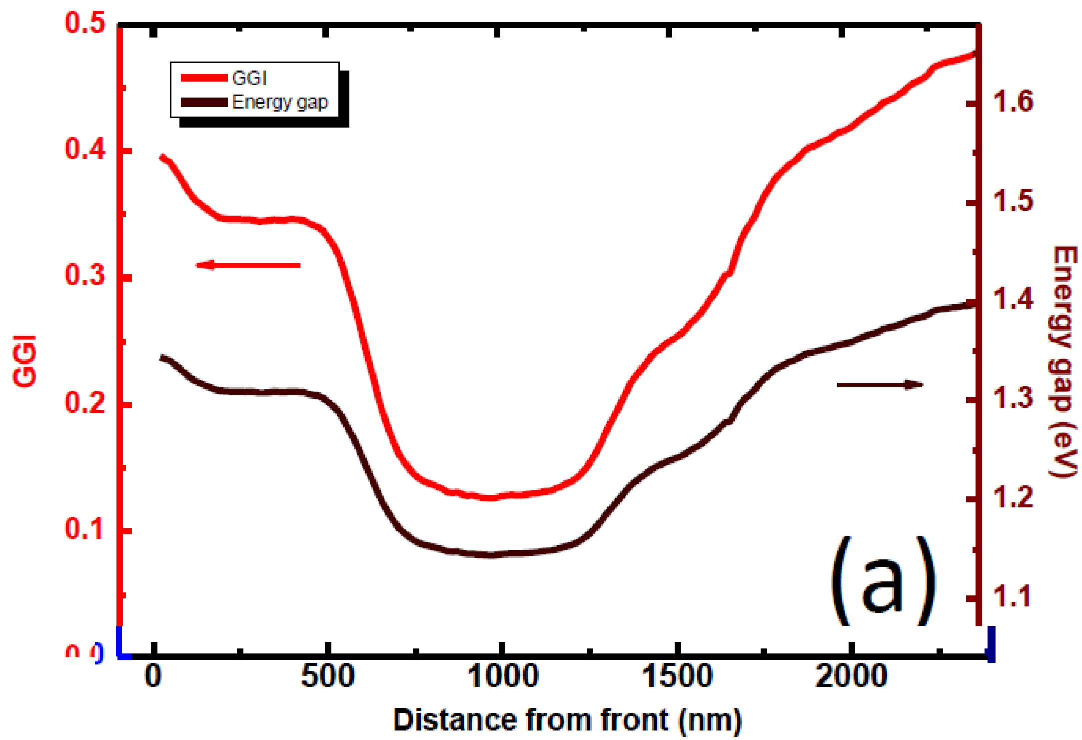
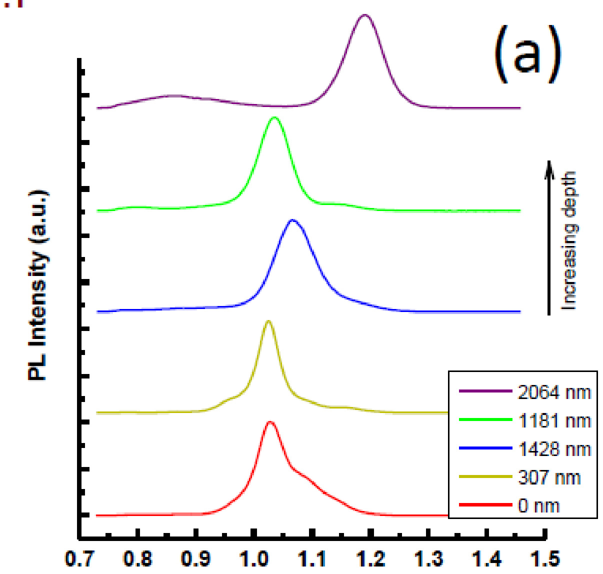
CIGS



Simulations performed considering the presence of a defective layer at the interface between CIGS and CdS

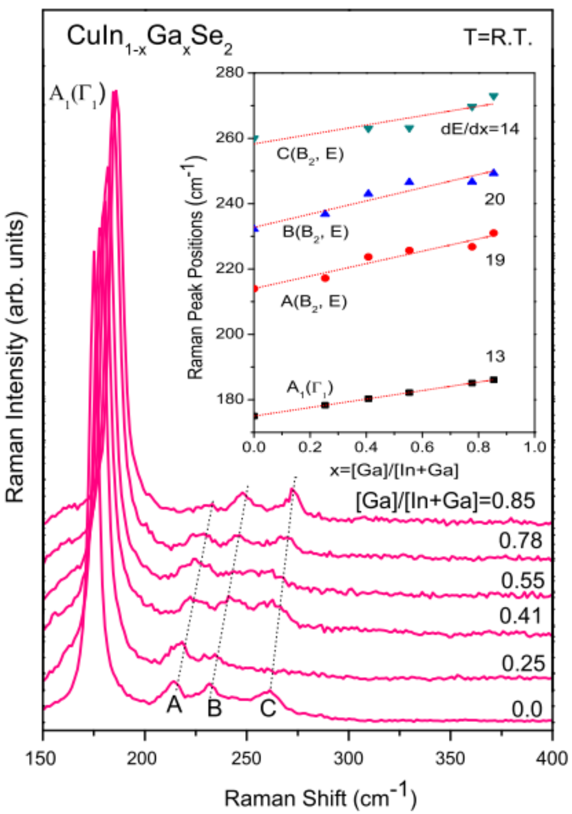


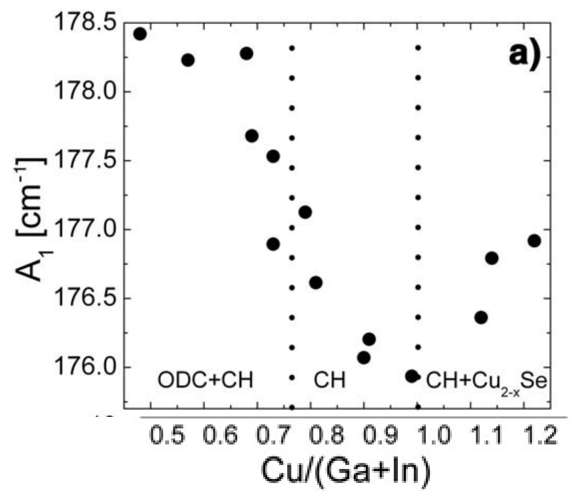

GGI
Energy gap
0.5
0.4
0.3
0.2
0.1
1.6
1.5
1.4
1.3
1.2
1.1
GGI
Energy gap (eV)
(a)
0
500
1000
1500
2000
Distance from front (nm)

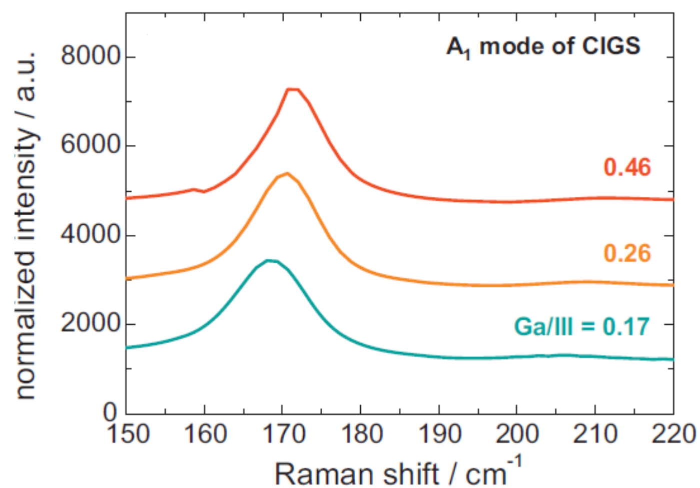

(a)
PL Intensity (a.u.)
Increasing depth
2064 nm
1181 nm
1428 nm
307 nm
0 nm
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5

Raman spectroscopy in CIGS

- The main Raman mode A1 (vibration of the Se anions in the x-y plane with the cations at rest) increases linearly with increasing Ga content (from 174 cm^{-1} for CIS to 184 cm^{-1} for CGS): its position can be used to make a quantitative estimation of the mean [Ga]/[Ga]+[In] and its depth gradient – and depends on the relative Cu content
- a shoulder at 150–170 cm^{-1}, is attributed to the OVC (ordered vacancy compound) phase



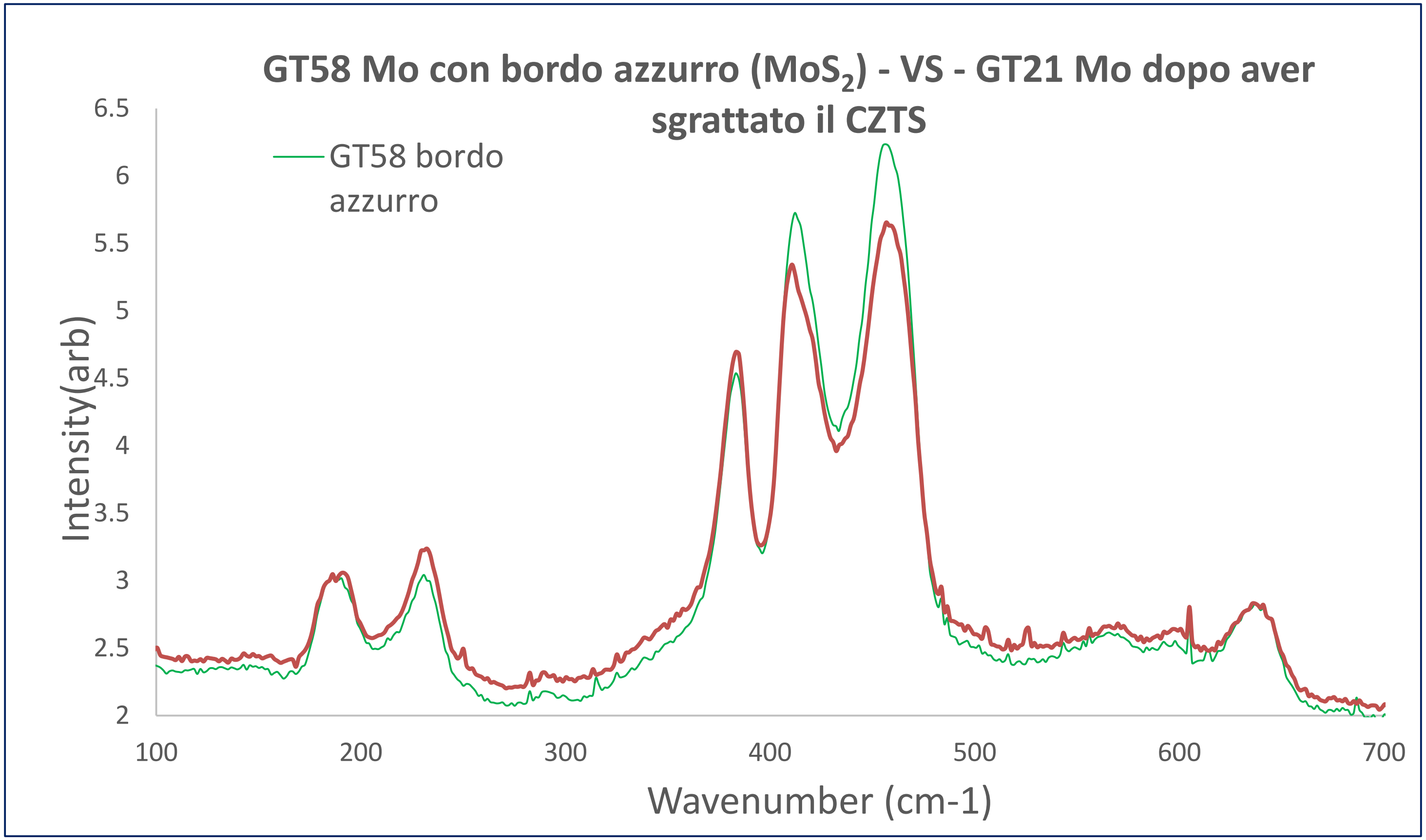




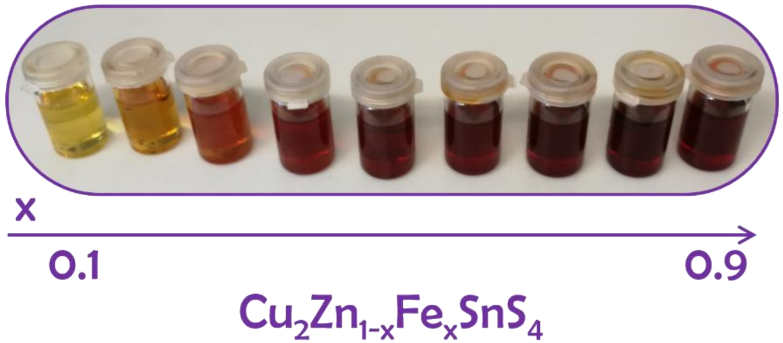
W. Witte et al . Thin Solid Films 517 (2008) 867–869;

Park et al., J. of Alloy and Comp. 513 (2012)068

MoS_2 on the back conctac

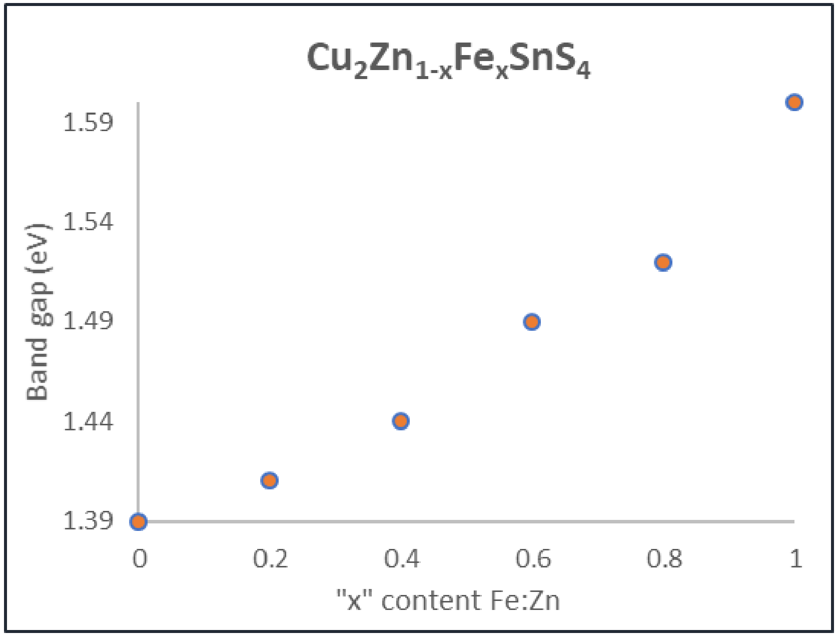


Tuning the gap by $Cu_2Zn_{1-x}Fe_xSnS_4$

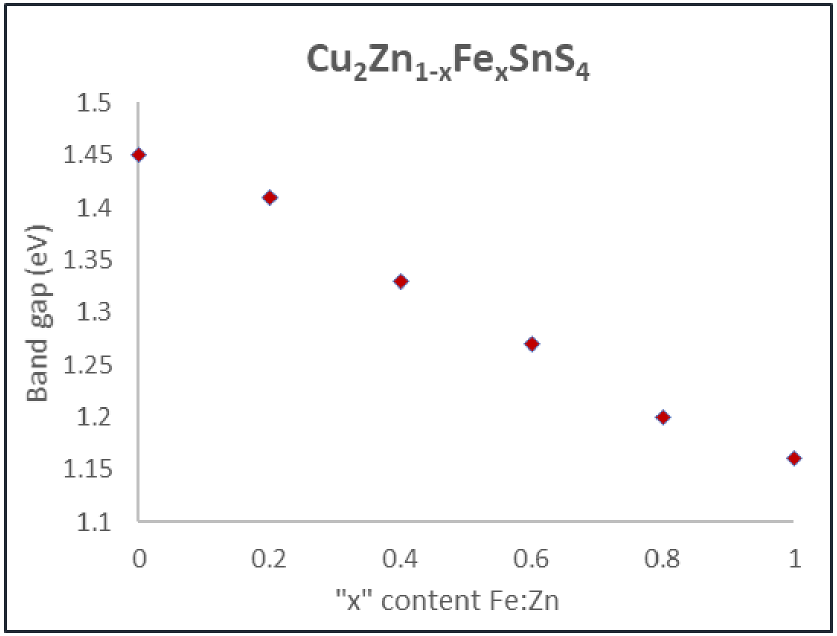


CZFTS

Unpublished resuts



Working in inert atmosphere

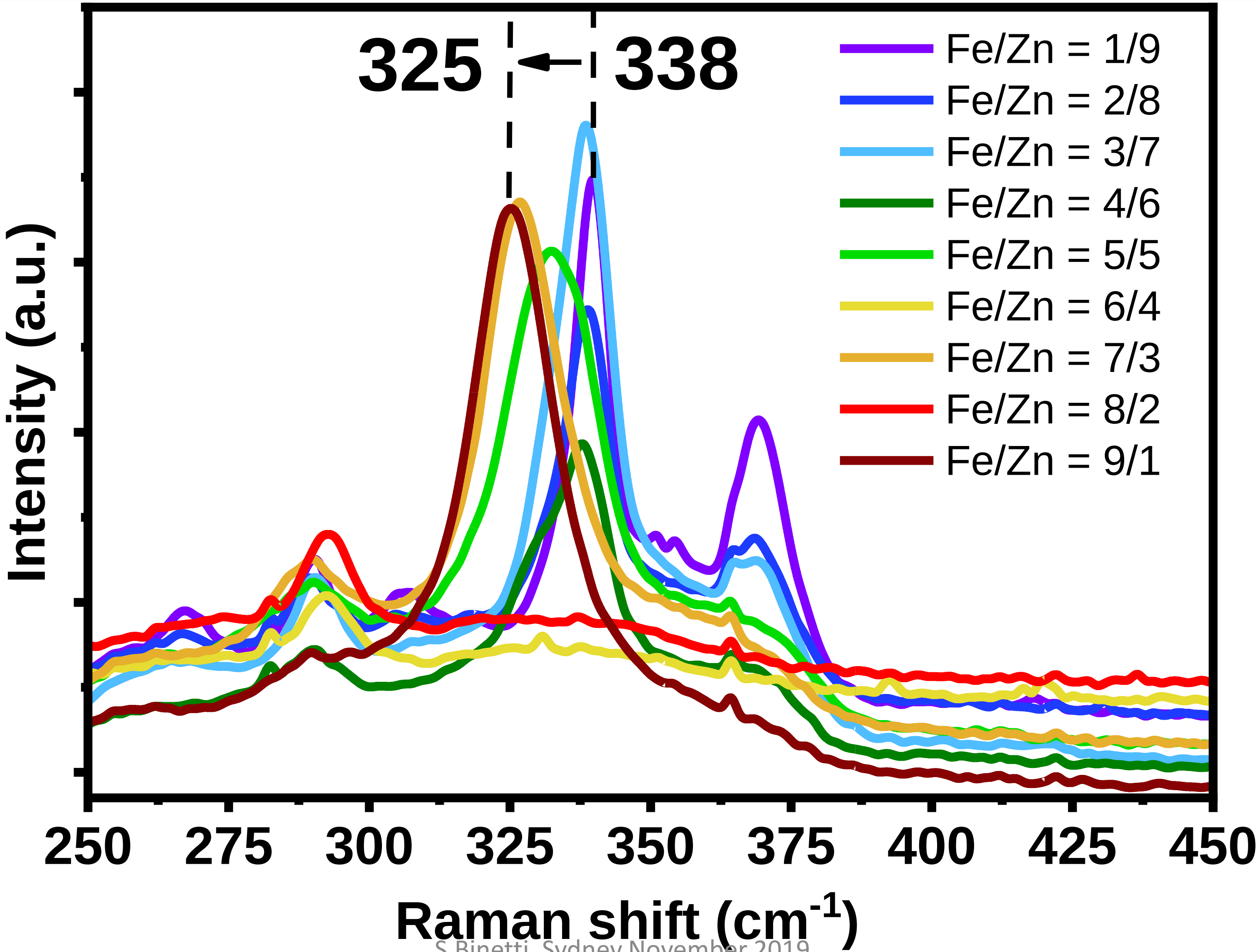


Working in air

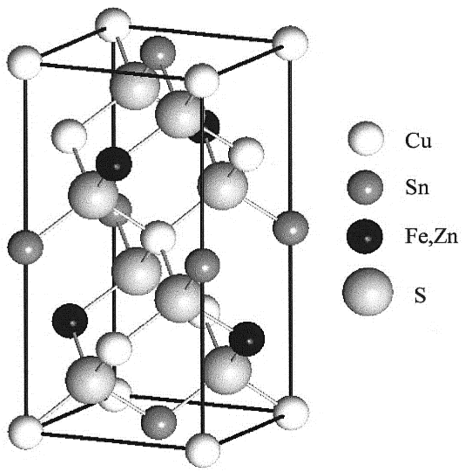
In agreement with J.Phys Chem 118 14227

Gel formation in situ

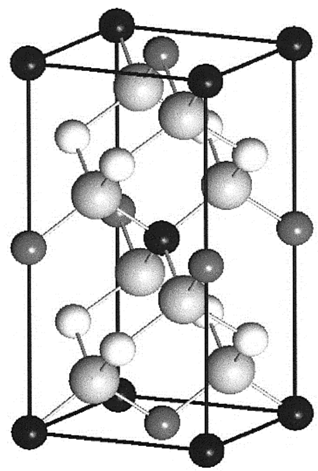
$Cu_2(Zn,Fe)SnS_4$



Tuning the gap $Cu_2Zn_{1-x}Fe_xSnS_4$

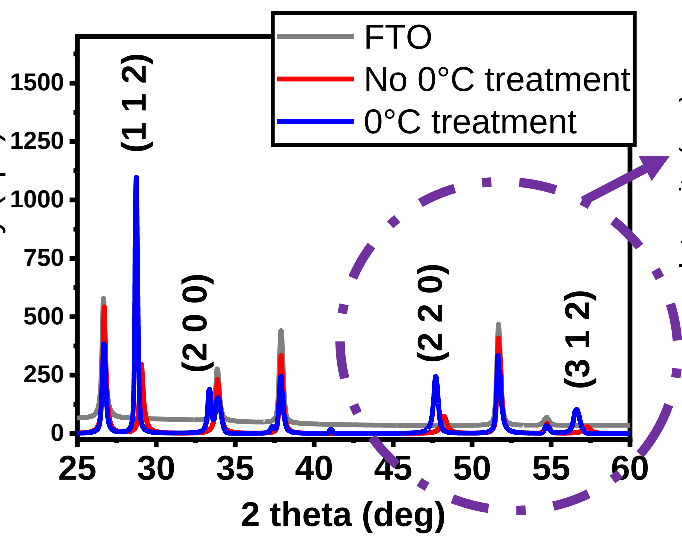


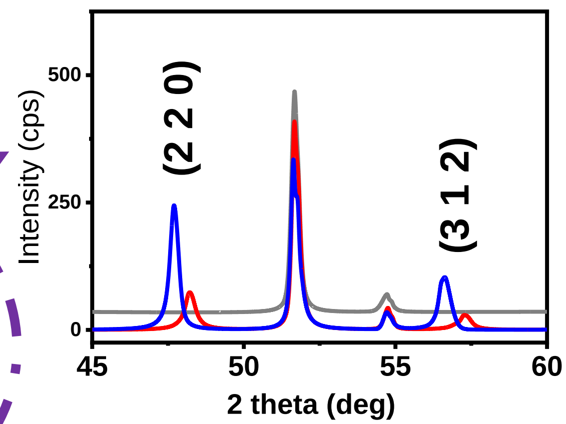
Kesterite

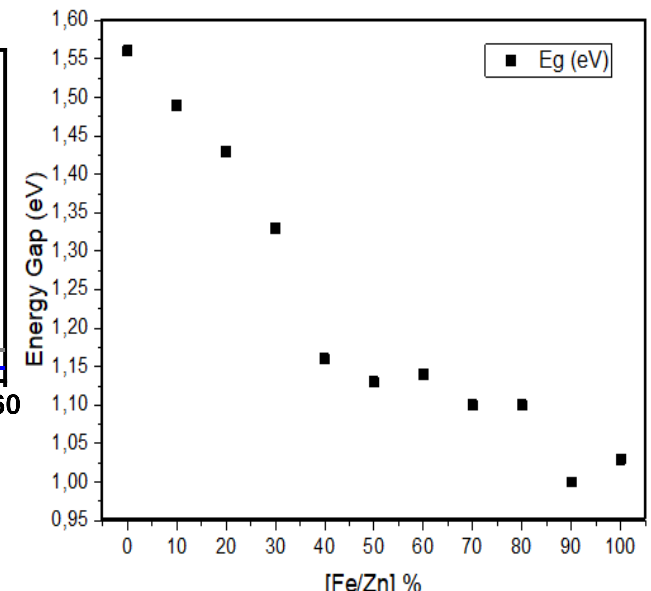


Stannite Cu_2FeSnS_4

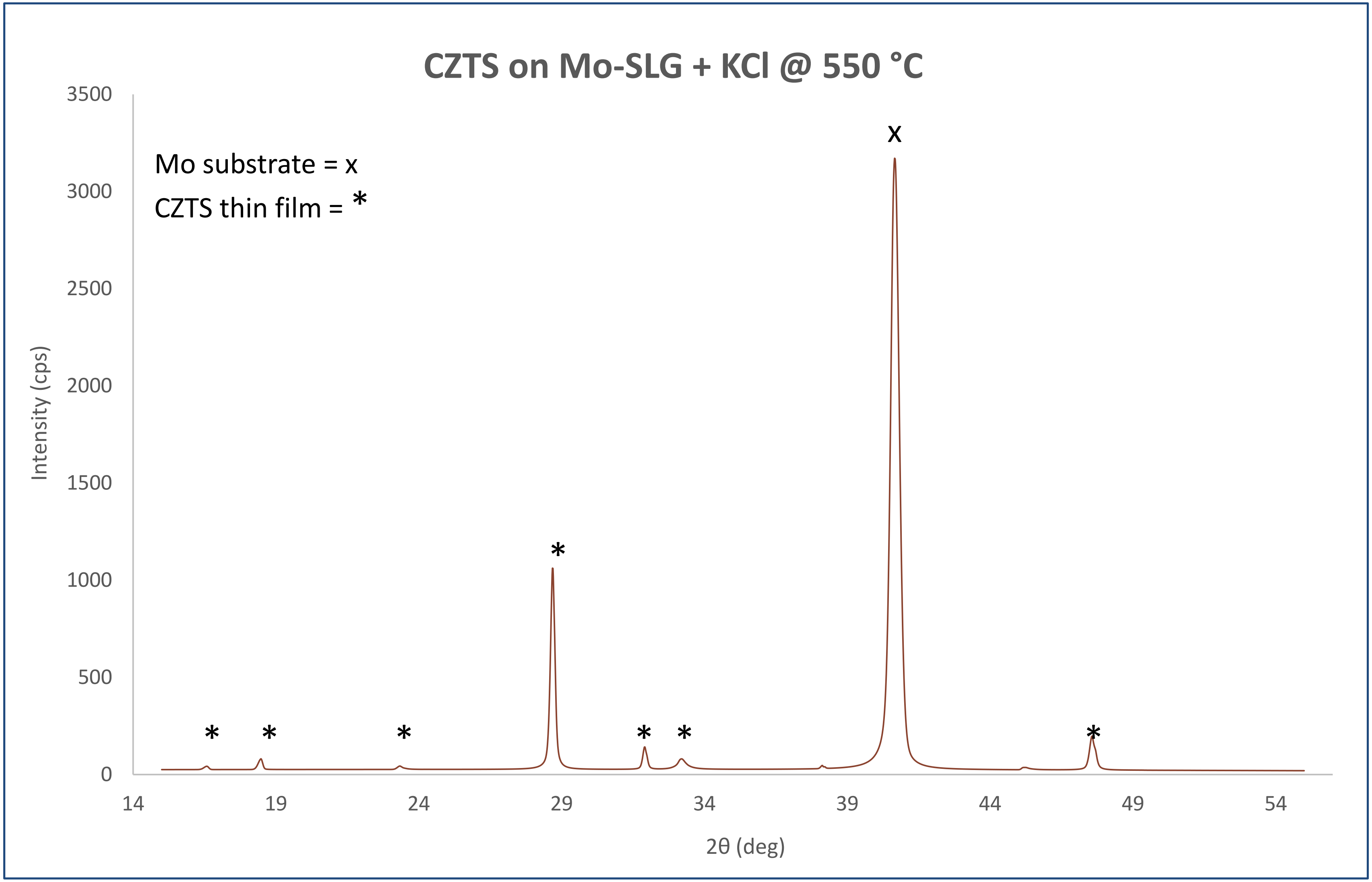
We were able to grown Cu_2FeSnS_4 thin-films in kesterite structure, adding a treatment at 0°C after spreading the Ink on FTO.





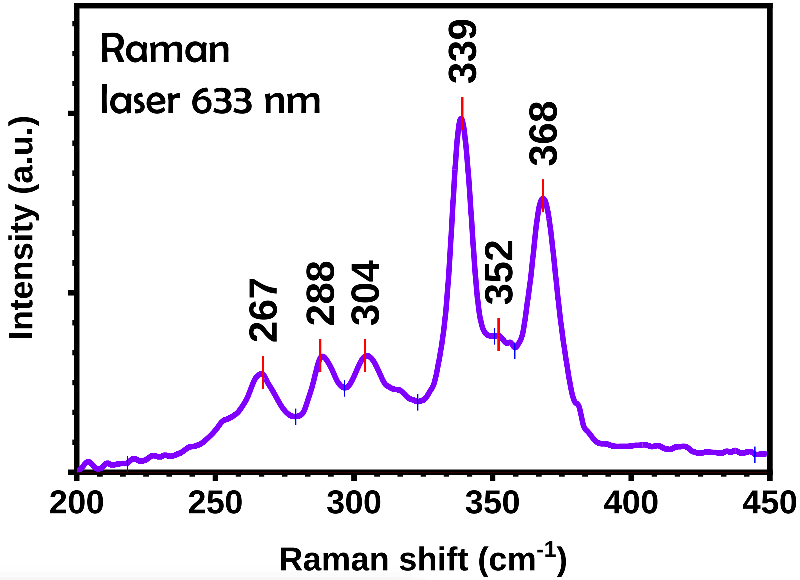


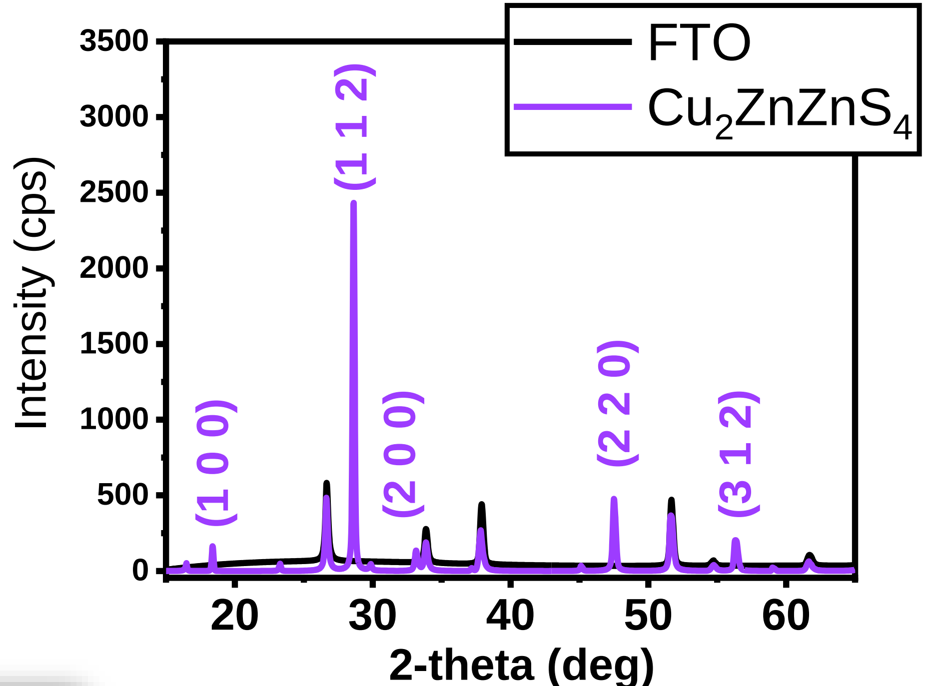
XRD phase analysis:

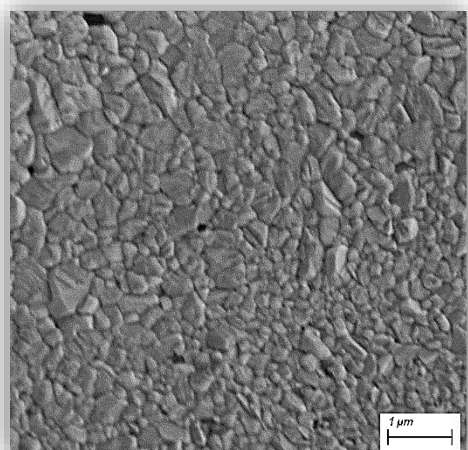


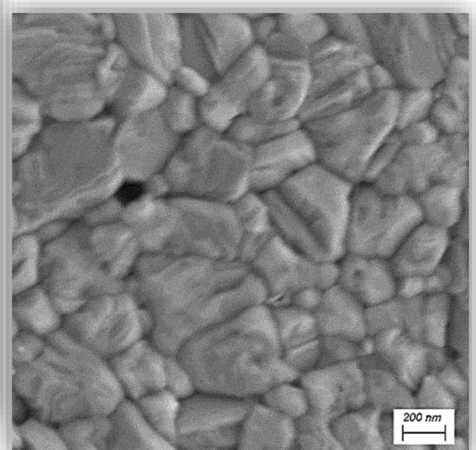
CZTS well-defined peaks with no secondary phases.

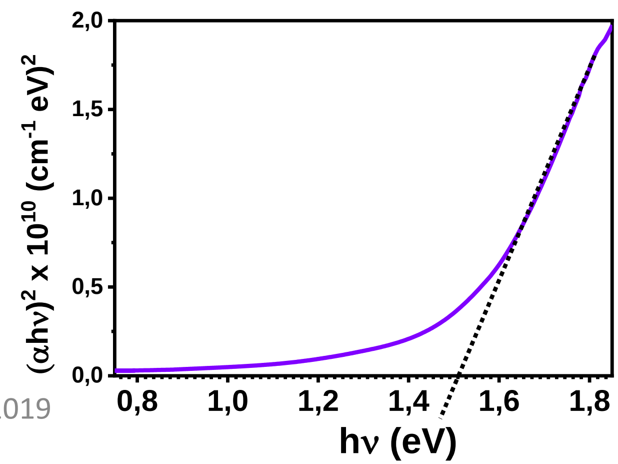
Gel formation in situ Cu_2ZnSnS_4







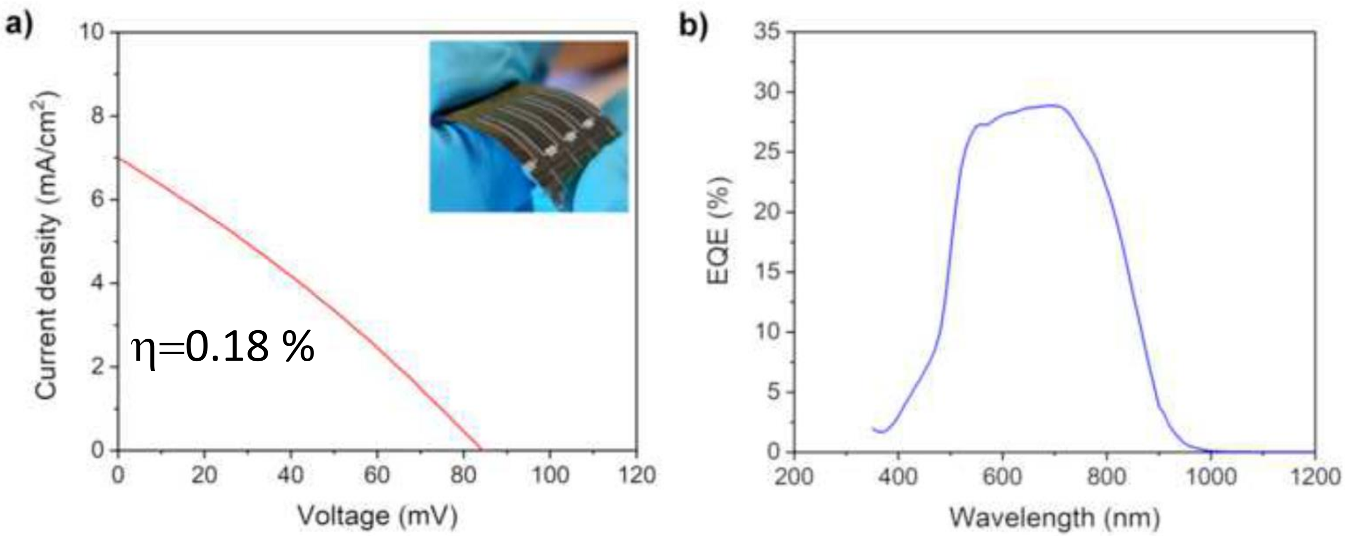


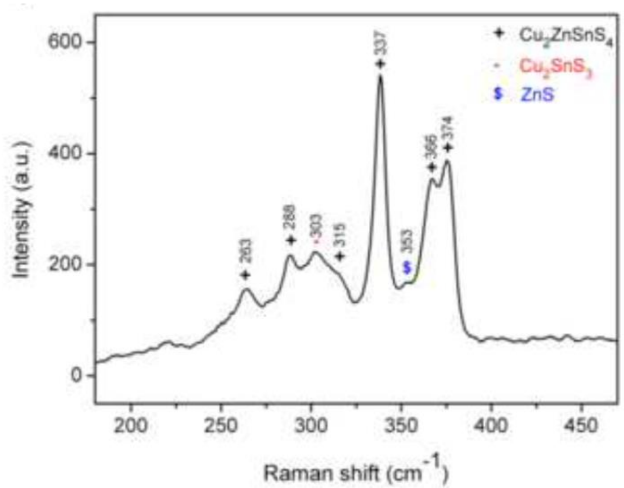


CZTS by electrodeposition

Co-electrodeposition of Cu-Zn-Sn (CZT) from alkaline solution on flexible Mo substrate followed by sulfurization

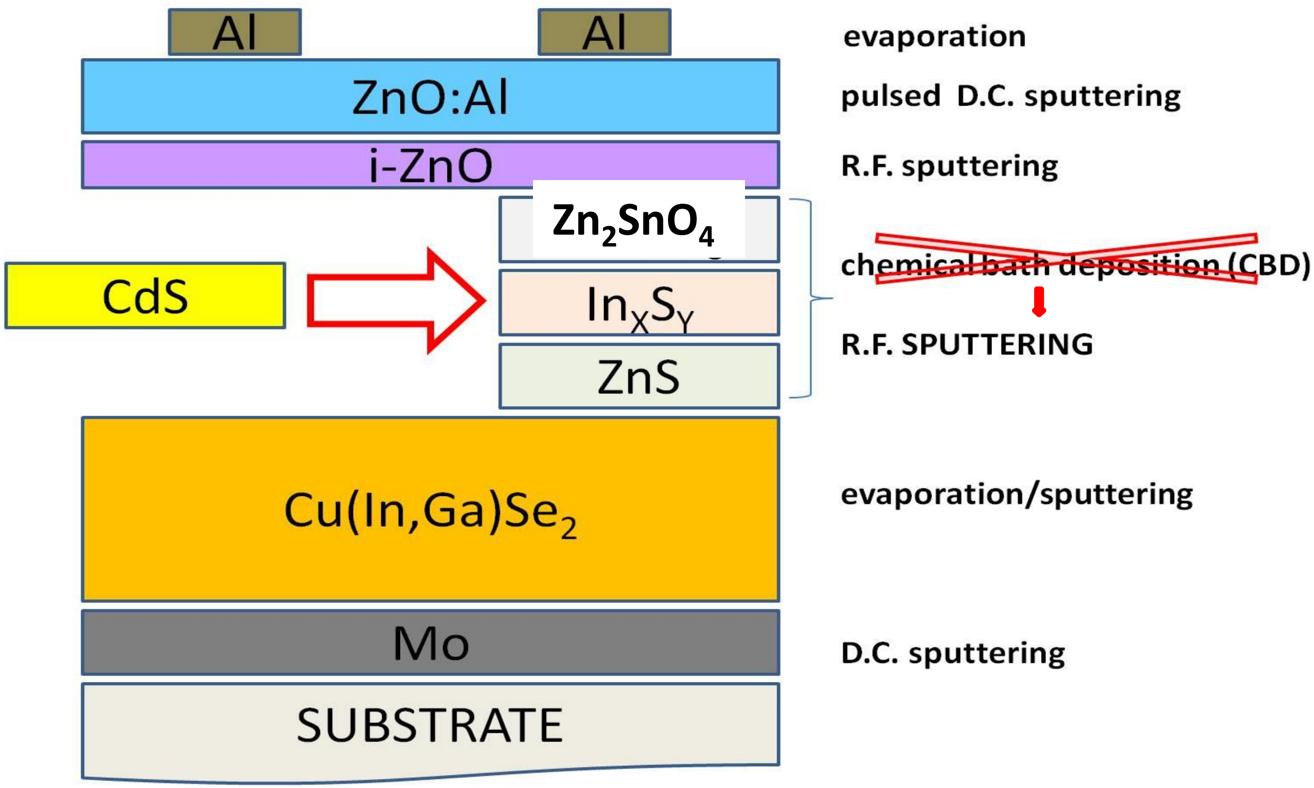
Potassium pyrophosphate (K4P2O7), CuCl2, ZnSO4·7H2O, EDTA-Na2 and SnCl2·2H2O in 100 ml of Millipore water





G. Marchi et al. Electrochemica act

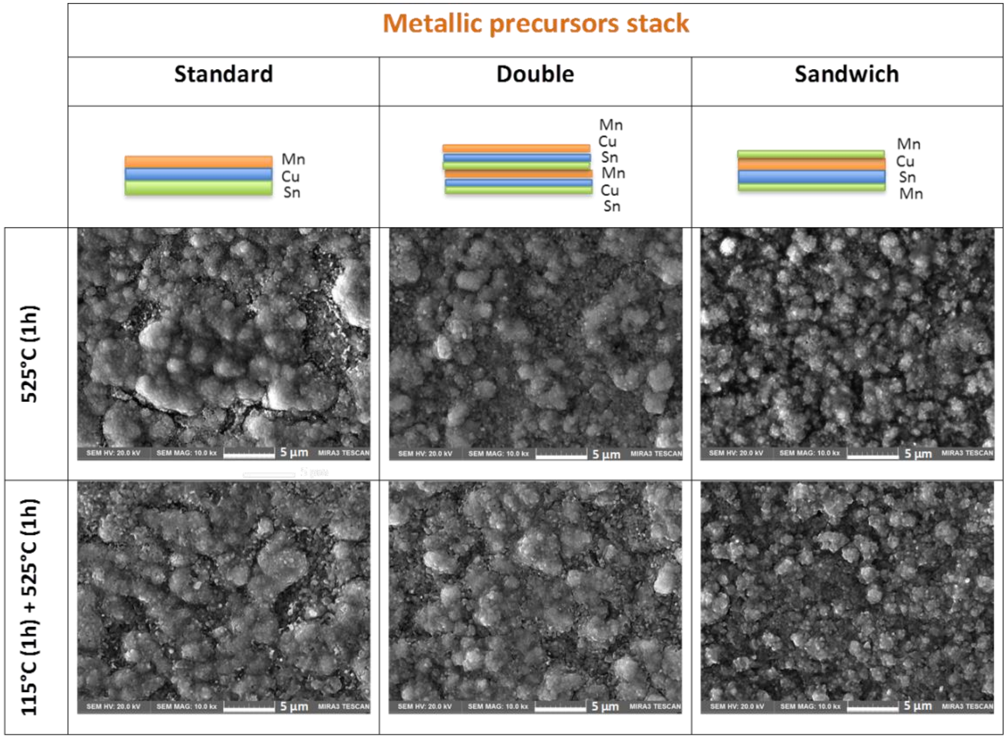
Cd-free alternative buffer layers for $Cu(In,Ga)Se_2$ and CZTS solar cells



The deposition of the ZTO films was operated both from a ceramic target (75wt% ZnO – 25wt%. SnO_2) and from two metal targets (Zn and Sn) to form a metal bi-layer followed by an oxidation

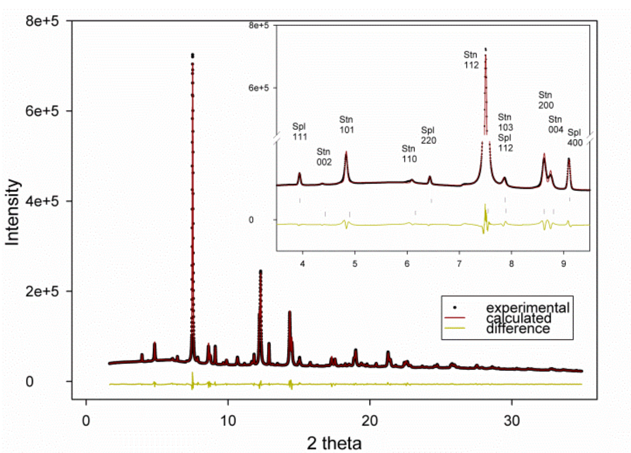
R.A. Mereu, A. Le Donne, S. Trabattoni, M. Acciarri, S. Binetti, Journal of Alloys and Compounds **626**, 112-117 (2015)

Cu_2MnSnS_4: 2nd Series (VS metals sequence and TT @ 115°C)



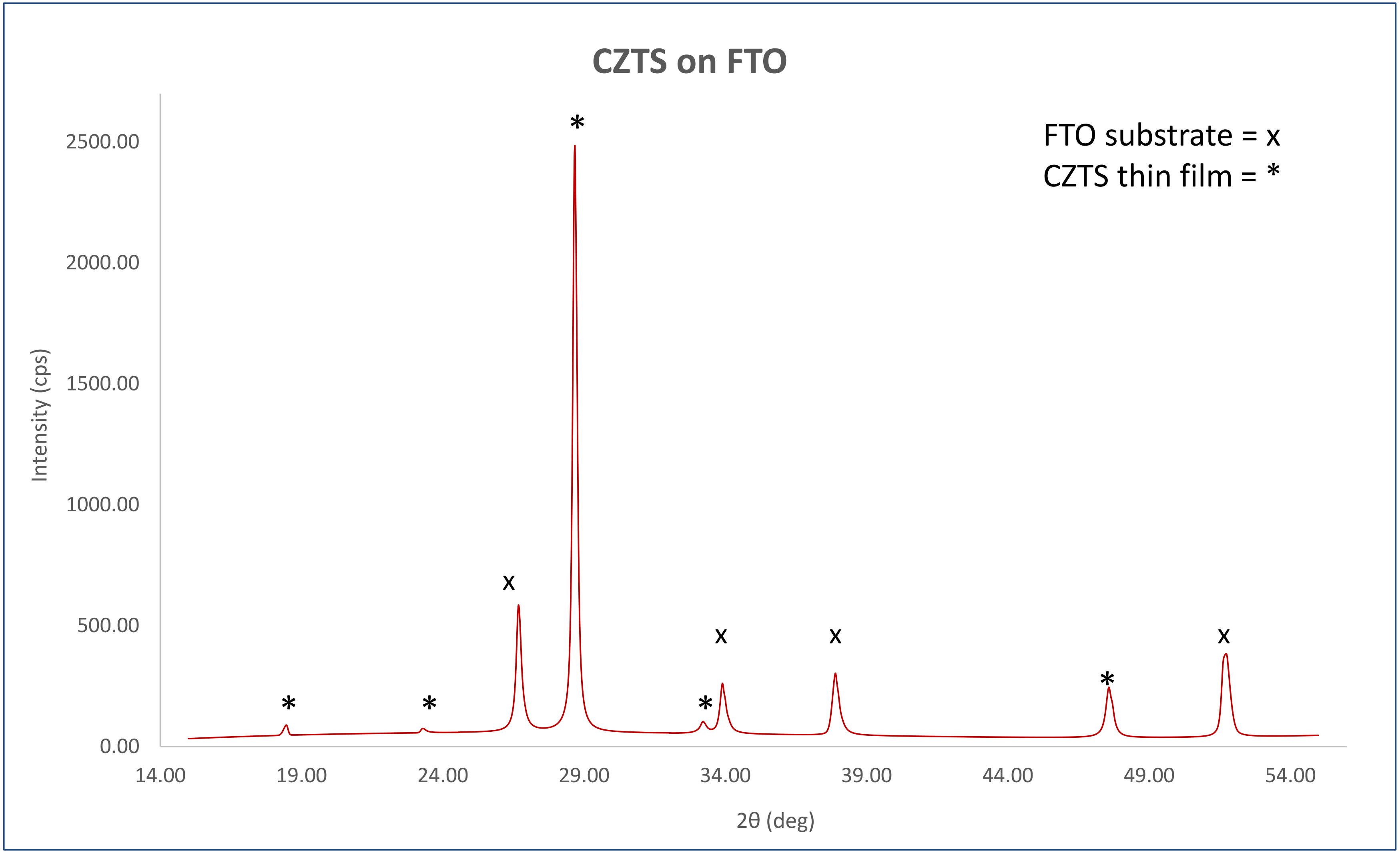
✓ the additional **step at 115°C** is mandatory to obtain larger grains, whose size seems to be almost constant for T > 525°C

✓the **sandwich stack** structure provided the best morphology in terms of compactness and grain size, but also the higher content of insulating spinel secondary phase ⇒ the **standard stack** structure provided the best compromise.

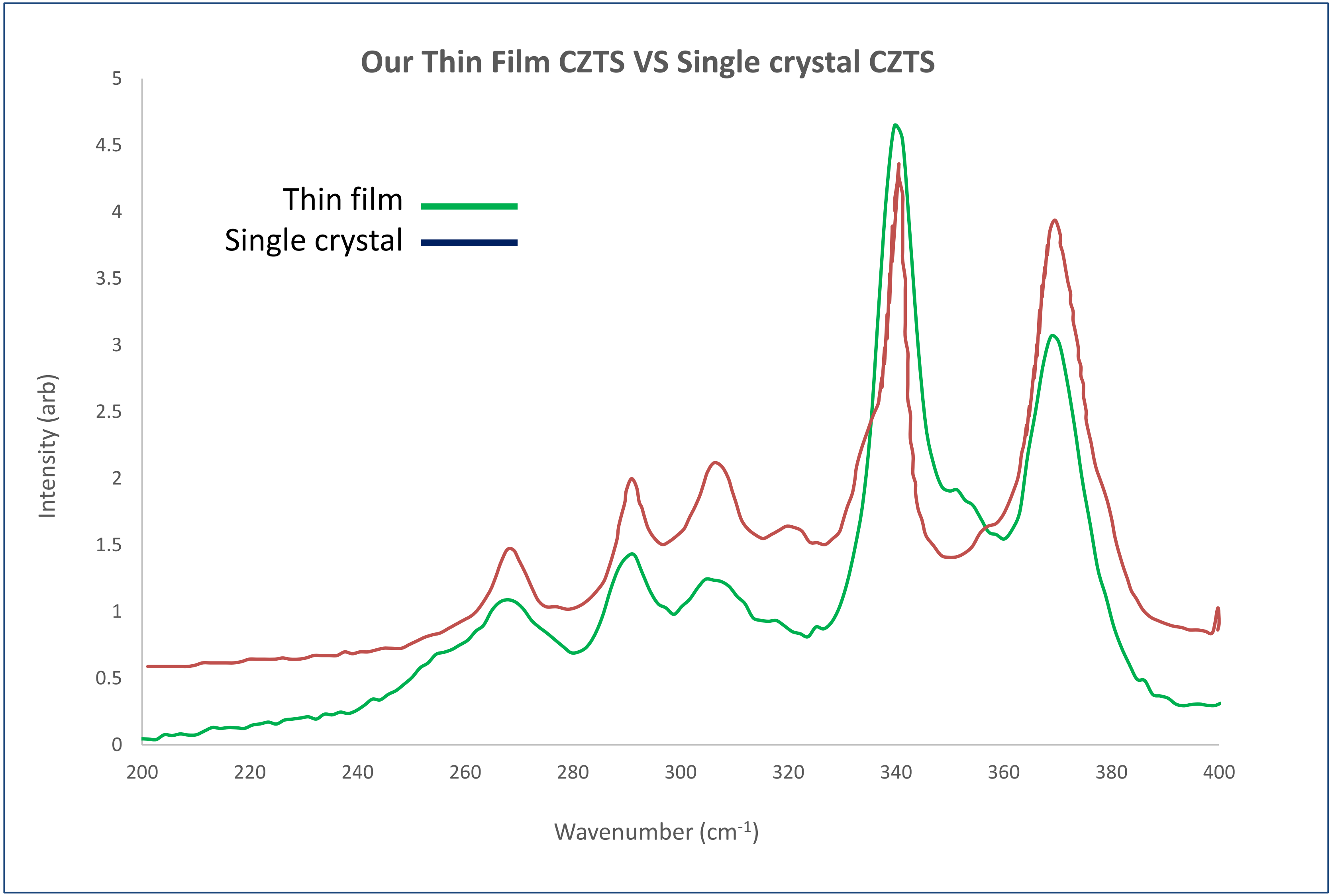


Stack structure	Sulfurization temperature	Cell parameters [Å] from XRD analysis			c/a ratio	[Stannite]/[Spinel] ratio
		a	b	c		
Standard	150 +525°C	5.503	5.503	10.855	1.972	89.05%
Double		5.489	5.489	10.823	1.972	87.96%
Sandwich		5.509	5.509	10.841	1.968	69.47%
Standard	150 +550°C	5.505	5.505	10.852	1.971	90.40%
Double		5.507	5.507	10.848	1.970	86.23%
Sandwich		5.511	5.511	10.836	1.966	76.22%
Standard	150 +585°C	5.507	5.507	10.847	1.970	90.71%
Double		5.509	5.509	10.845	1.968	90.15%
Sandwich		5.512	5.512	10.837	1.966	81.90%

	Raman Shift (cm^{-1})
CZTS	266, 288, 338, 368-374
Cu_2SnS_3	295-303, 355
SnS_2	315
SnS	164, 192,218
ZnS	278, 351
Cu_2S	264, 475

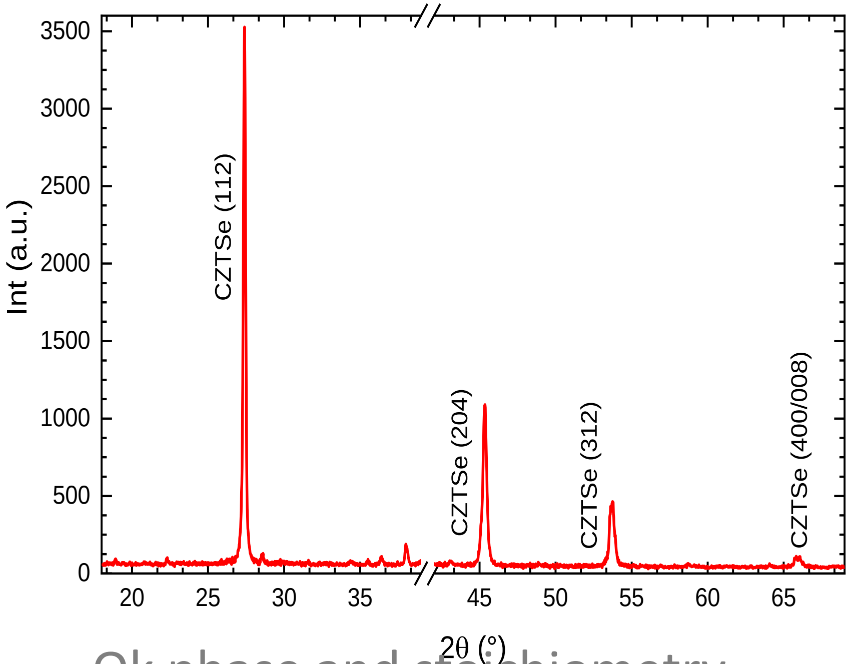

CZTS on FTO
FTO substrate = x
CZTS thin film = *
Intensity (cps)
2500.00
2000.00
1500.00
1000.00
500.00
0.00
14.00
19.00
24.00
29.00
34.00
39.00
44.00
49.00
54.00
2θ (deg)
*
*
x
*
*
x
x
*
x

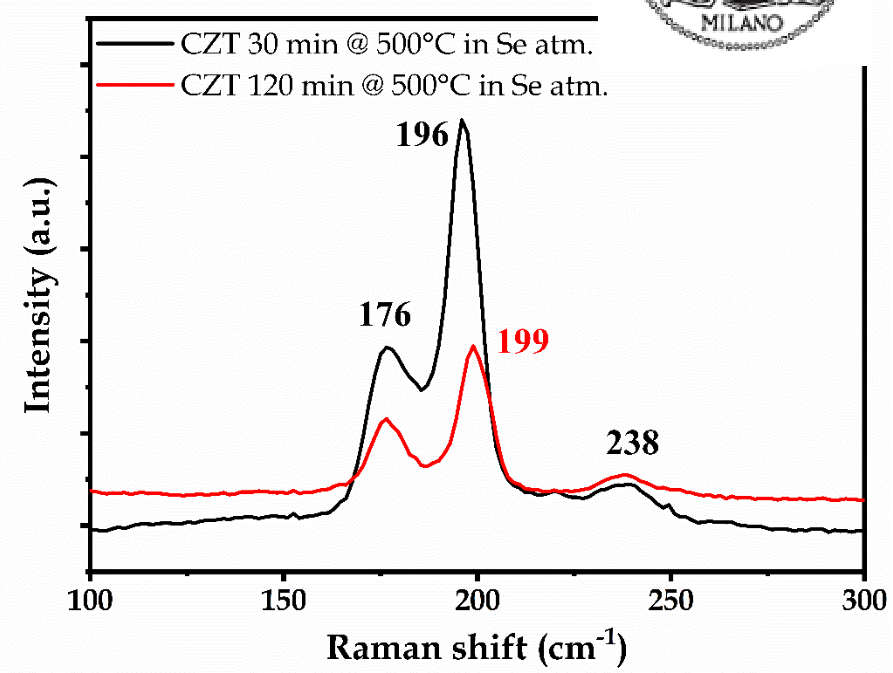
Raman spectrum:



Well-defined peaks, comparable with single crystal XRD!

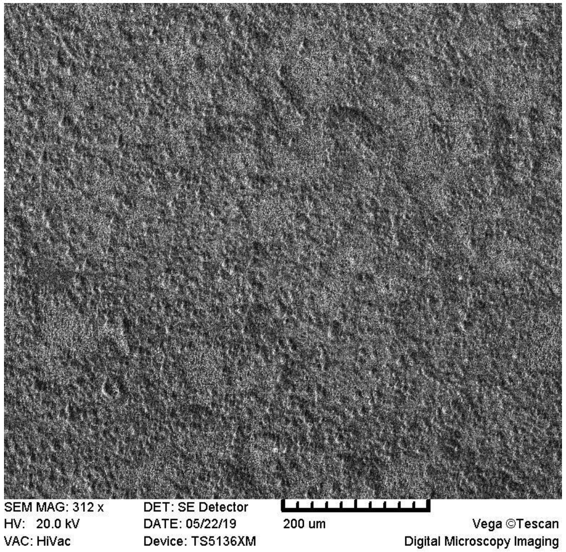
CZTSe electrodeposition sample : preliminary results



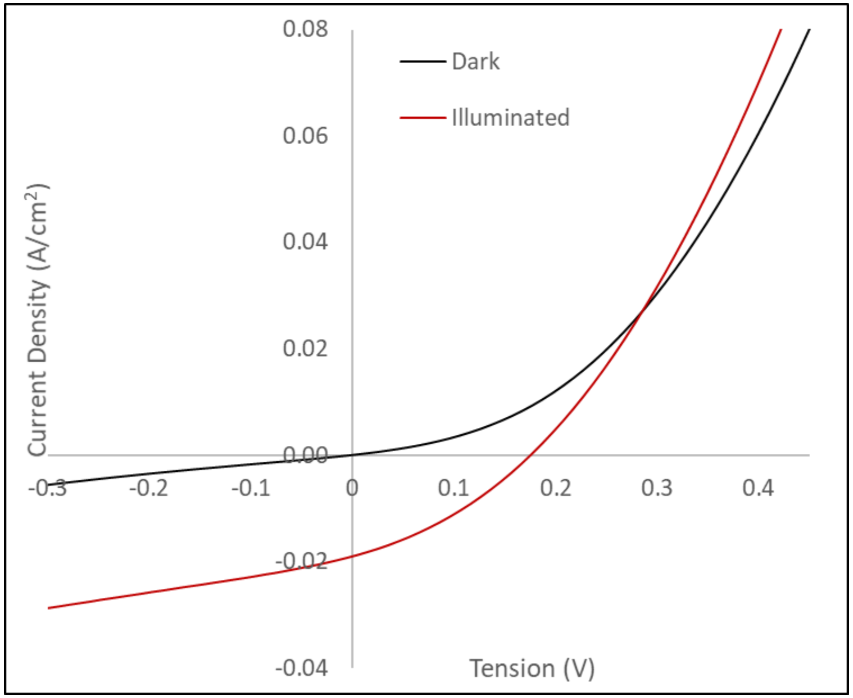


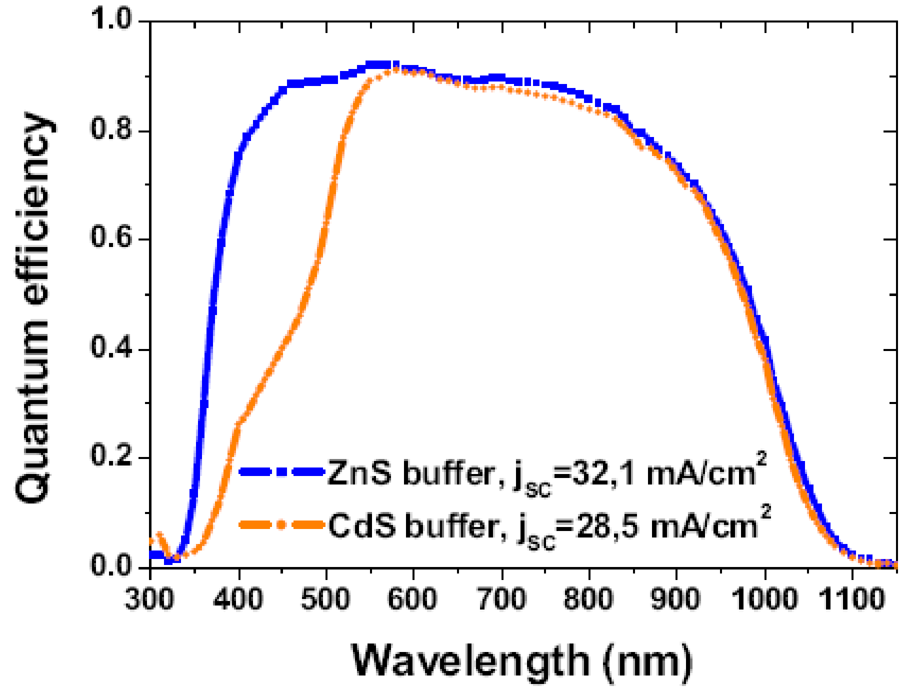
Ok phase and stoichiometry

➔ Good homogeneity



Device Per





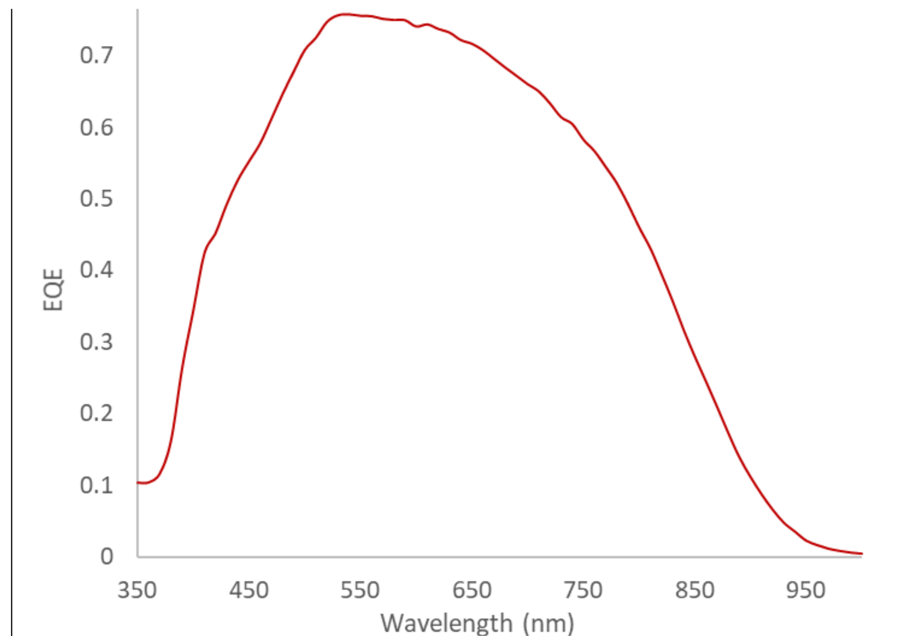
V_{oc} = 175.0 mV → **Modest V_{oc}**

J_{sc} = 18.93 mA/cm^2 → **Respectable J_{sc}**

η = 1.11 %

FF = 33.43 %

SCAPS software simulation confirms problems at the interface with the back contact

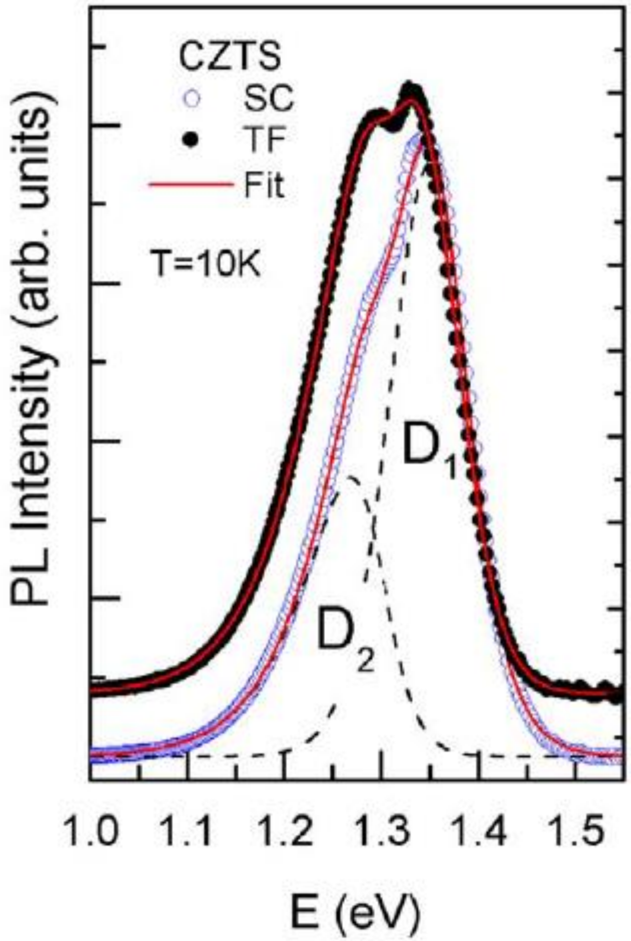


G. Tseberlidis, V. Trifiletti et al., Manuscript in preparation 2019

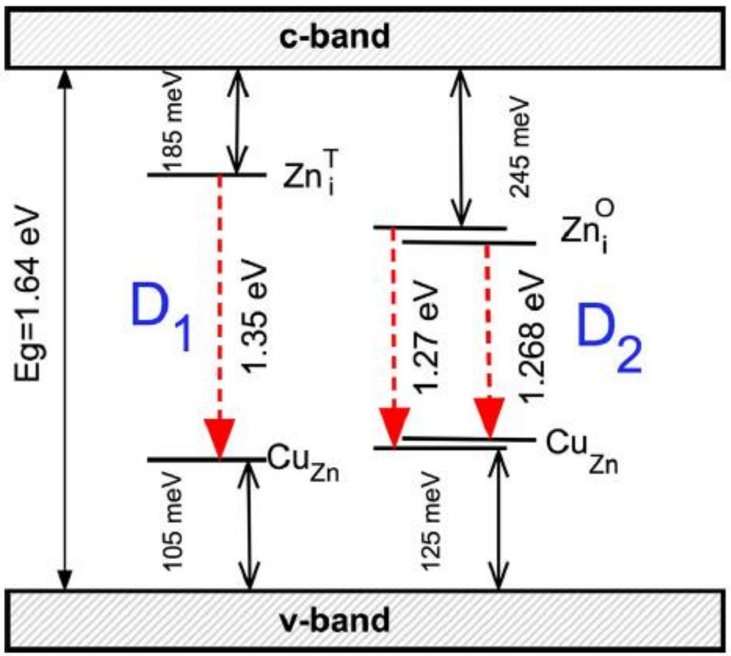
PL results

Togliere

Thin film (TF) compared with Single Crystal (SC) kesterite



These bands could be related to deep donor-deep acceptor (DD-DA) complex defect

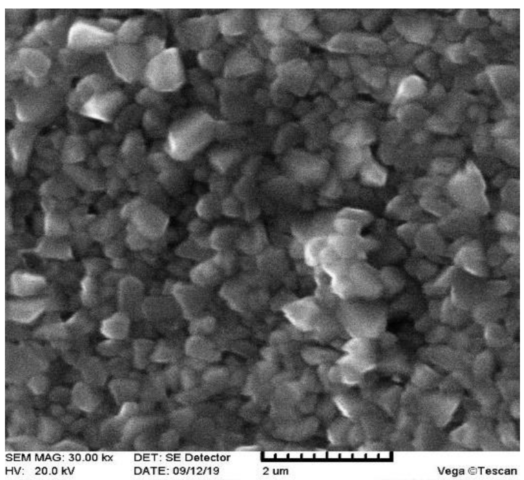


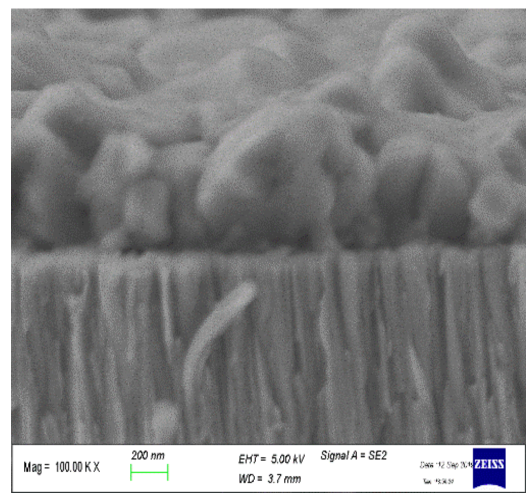
The presence of Zn_i must be reduced

J.Krustoka, T.Raadik, M.Grossberg, V. Trifiletti, S.Binetti,
Materials Science in Semiconductor Processing , 80, 52 (2018)

Optimization of the solution

Entry#	Cu/(Sn+Zn)	Zn/Sn	Thiourea [conc.]	Voc (mV)	Jsc (mA/cm^2)	FF %	η %
1	1.00	1	3.7 M	-	-	-	-
2	0.91	1	3.7 M	-	-	-	-
3	0.86	1	3.0 M	-	-	-	-
4	0.83	1	3.0 M	83.0	8.0	29.1	0.18
5	0.80	1	3.0 M	70.0	11.6	26.2	0.21
6	0.80	1.1	3.0 M	149.4	12.6	31.0	0.58
7	0.80	1.2	3.0 M	175.0	18.9	33.4	1.11
8	0.80	1.2	2.3 M	60.0	7.6	27.0	0.12





G. Tseberlidis, V. Trifiletti et al., Manuscript in preparation 2019