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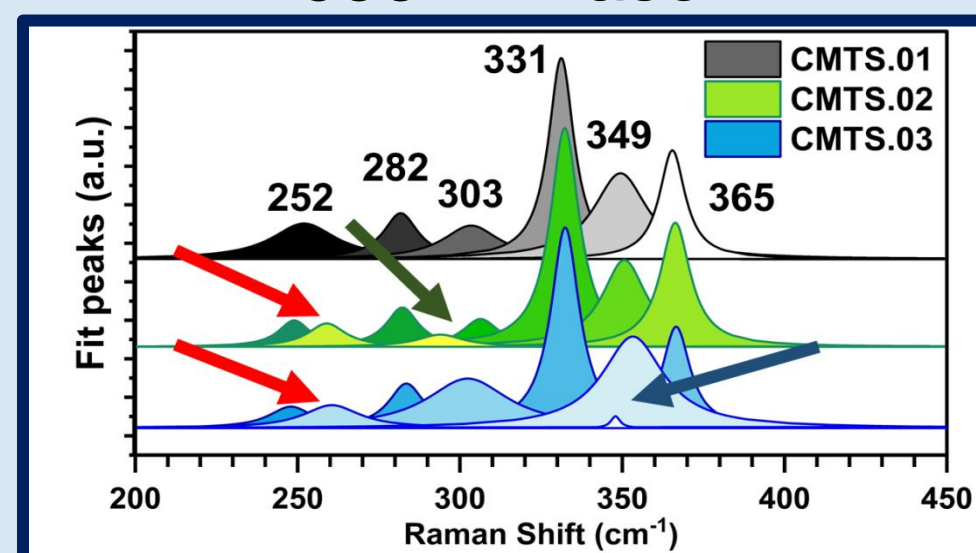
Thin film low-cost and eco-friendly photovoltaic devices are based on $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$. To reduce production costs and improve sustainability, manganese can substitute zinc since Mn is safe and Earth-abundant, and it can be used as a light absorber¹⁾ Here, we report on the growth and characterization of $\text{Cu}_2\text{MnSnS}_4$ thin films, produced both by a two-step deposition process and by a sol-gel-based method. The metallic precursors have been deposited by sputtering, and the stack annealed at high temperatures in sulphur atmosphere. The layers, obtained in a Cu-poor and Mn-poor compositional regime, have been tested in solar devices with a record efficiency of 1.13%, with an open-circuit voltage of about 445 mV, delivered after over one year from the first PV measurement. X-ray diffraction and photoelectron, Raman, photoluminescence, and admittance spectroscopies have been used to characterize $\text{Cu}_2\text{MnSnS}_4$, and a scenario of high defectivity has emerged.²⁾ Therefore, we moved to a sol-gel-based method, to improve the quality of the material reducing defectivity. An ink, prepared by dissolving in dimethyl-sulfoxide metal salts and thiourea, used as the only source of sulphur, was deposited by blade coating to obtain thin films. Sol-gel transition took place in air and then samples were annealed at 550°C under argon atmosphere. The so obtained thin films were fully characterized showing promising preliminary results.

1)Le Donne A. et al., Front. Chem, 2019, 7:297. 2)Trifiletti V. et al., Solar Energy Materials & Solar Cells, 2023, 254 112247.

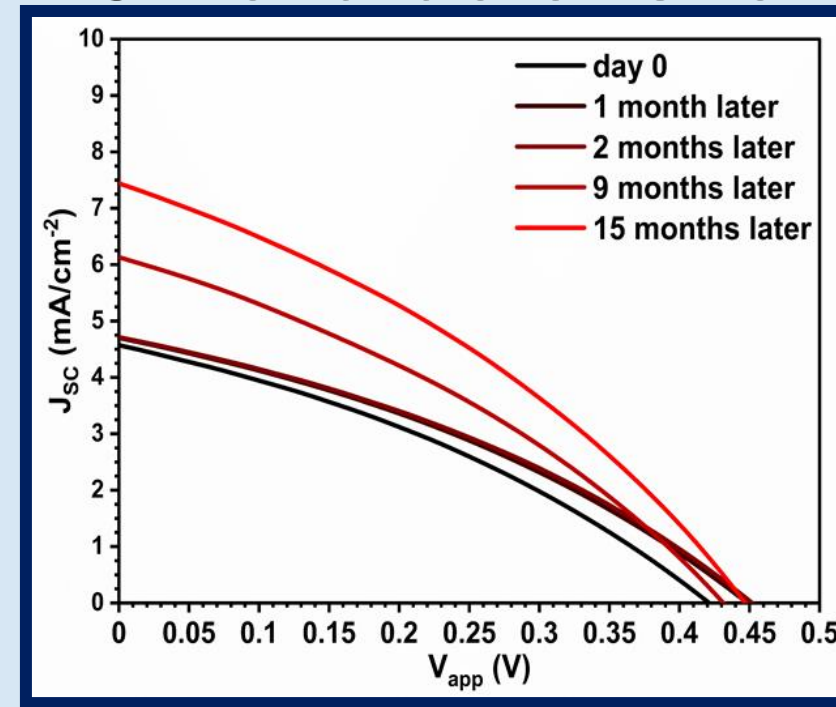
Mn
Cu
Sn
Mo
glass

- Annealing temperature: **570°C**
- Heating rate: **15 °C/min**
- Atmosphere: **S vapour in Ar**

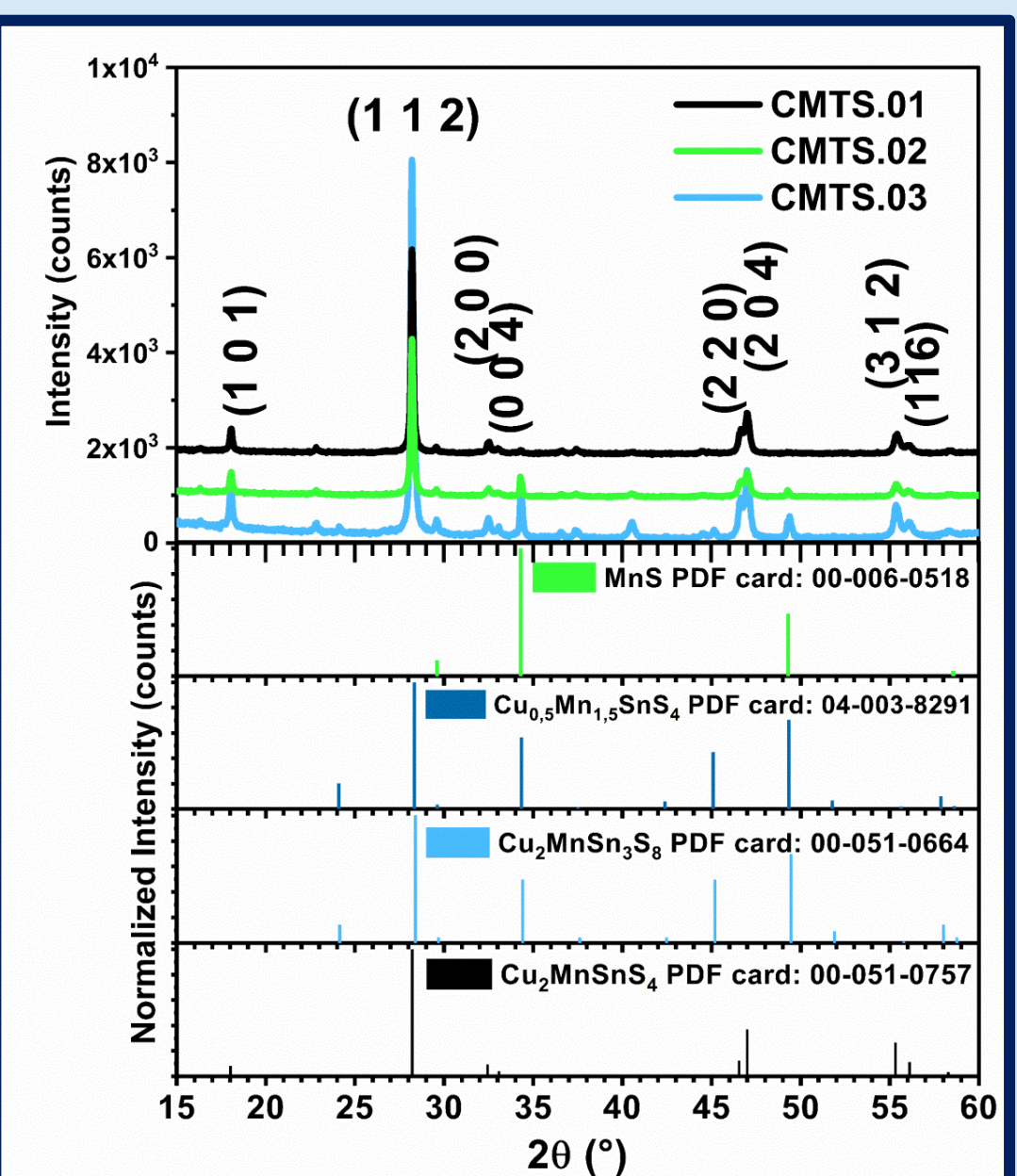
μ-Raman: 633 nm laser



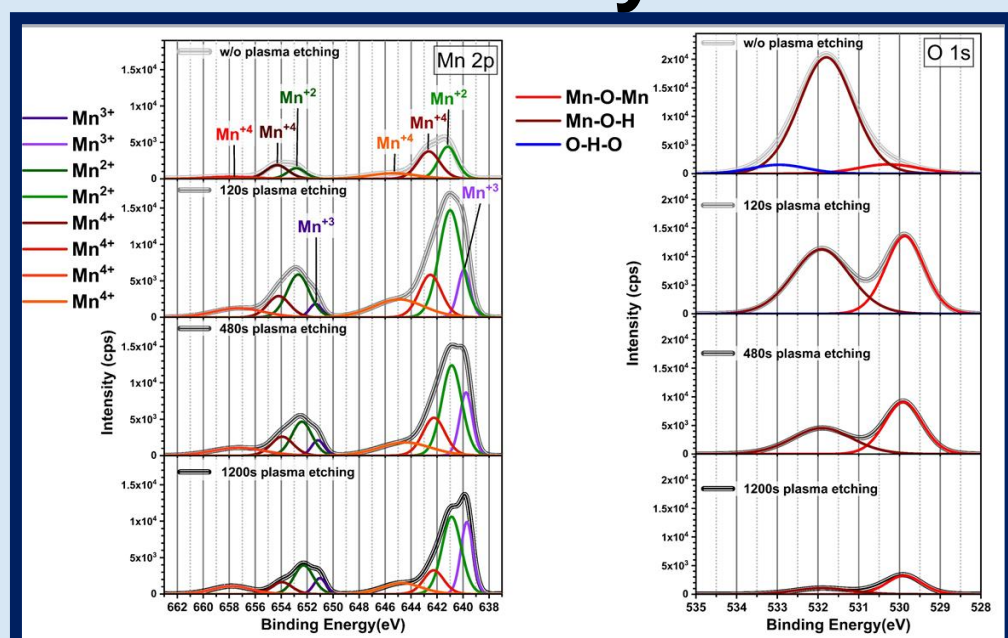
J-V characteristic



X-ray diffraction: performed on powders

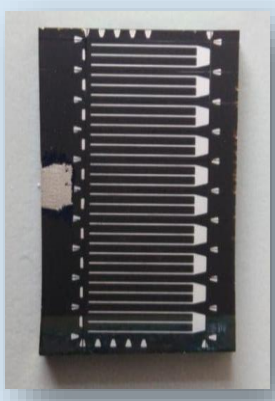


XPS analysis

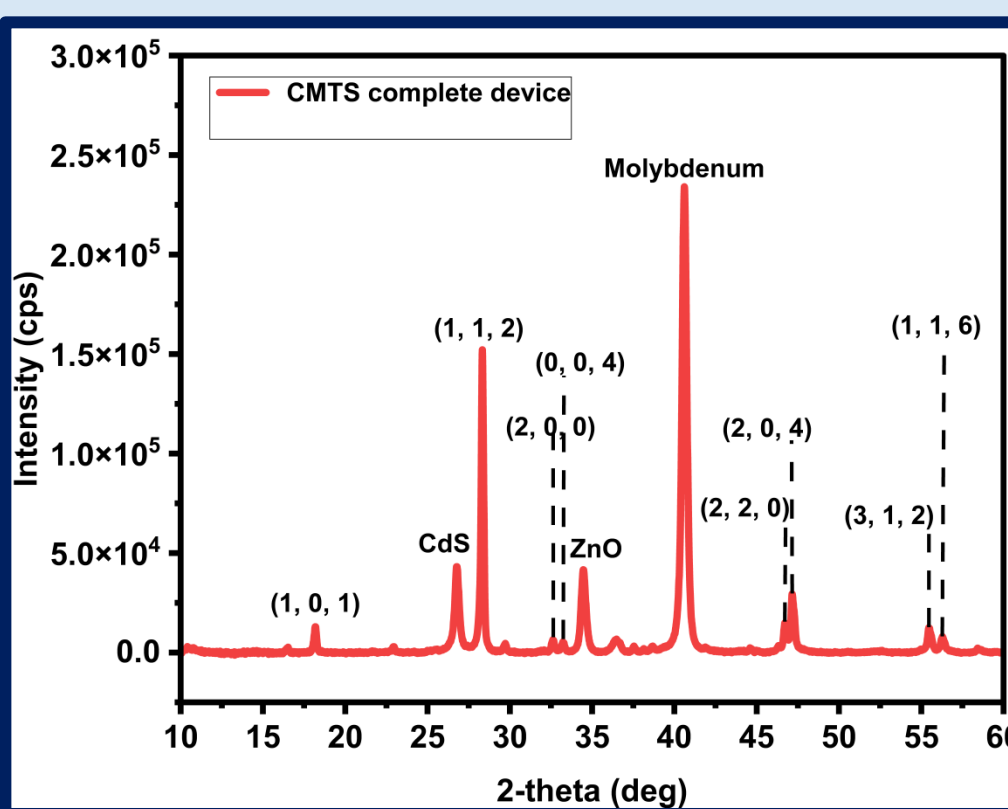


Parameters	Day 0	1 month	2 months	9 months	15 months
J_{sc} (mA/cm ²)	4.56	4.70	4.71	6.14	7.45
V_{oc} (mV)	420.4	447.8	451.1	430.9	444.8
FF	0.34	0.34	0.35	0.34	0.34
η (%)	0.65	0.72	0.74	0.89	1.13

Al
AZO
i-ZnO
CdS
CMTS
Mo
glass

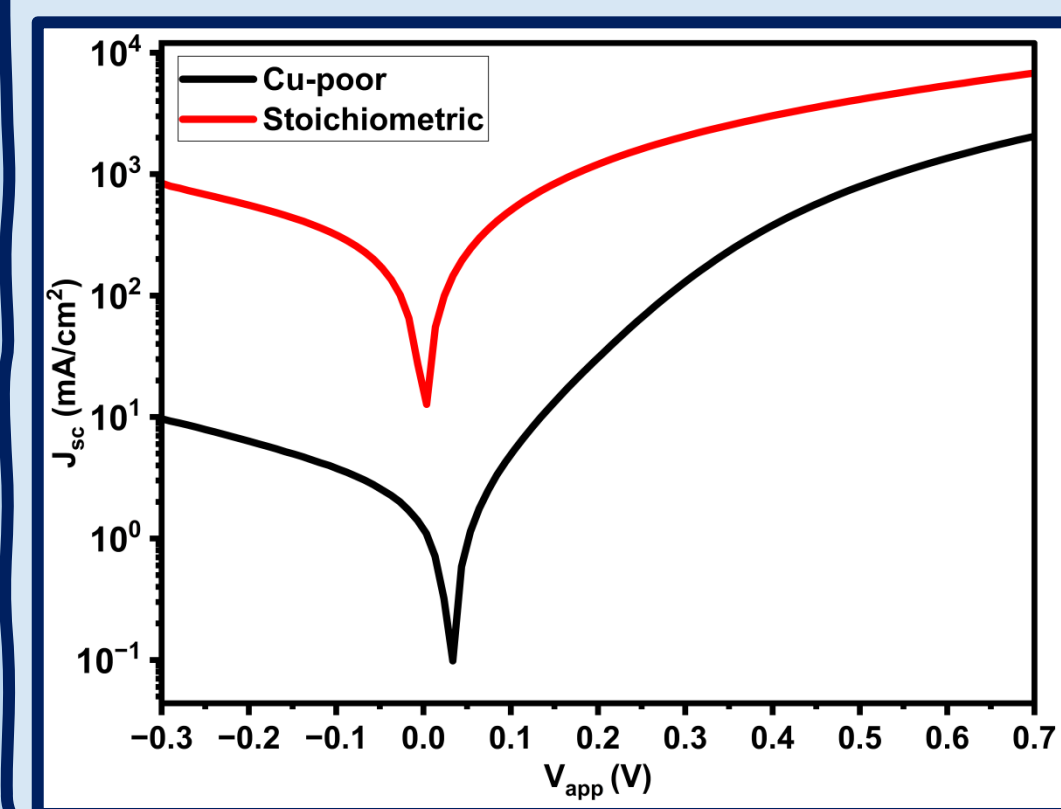


XRD diffraction



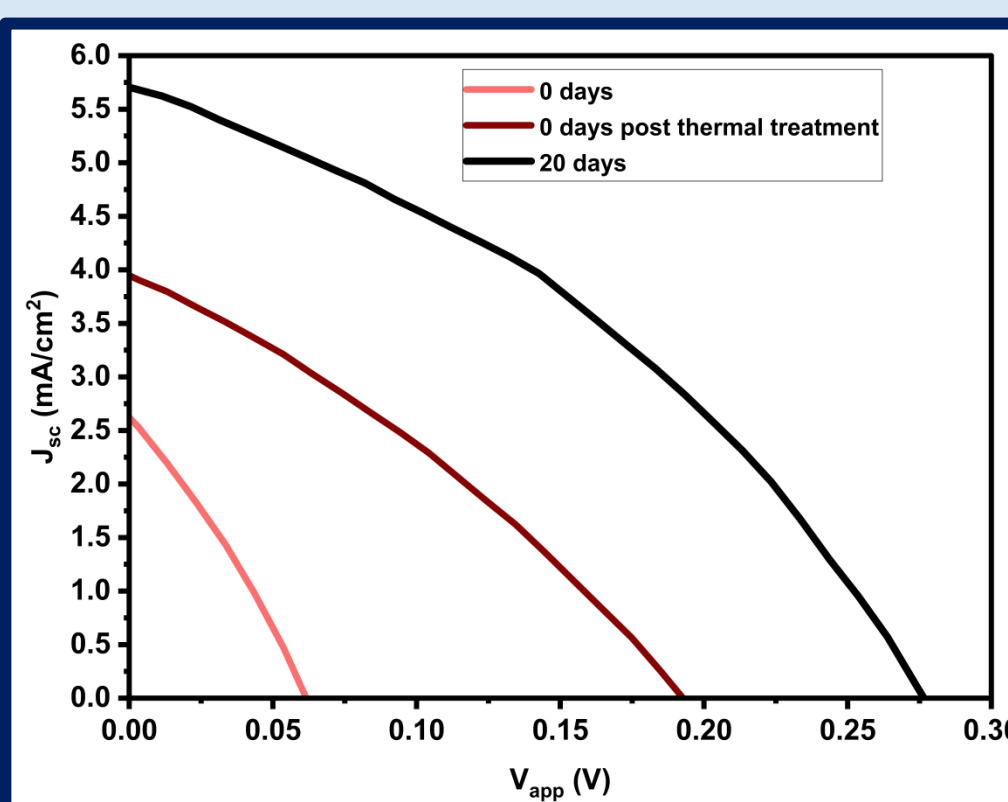
- Complete device:** identification of each layer
- High-purity CMTS phase** obtained

Metal ratio: dark curve



- Copper-poor conditions:** diode like behavior
- Stoichiometric conditions:** metal like behavior

Thermal treatment and aging:

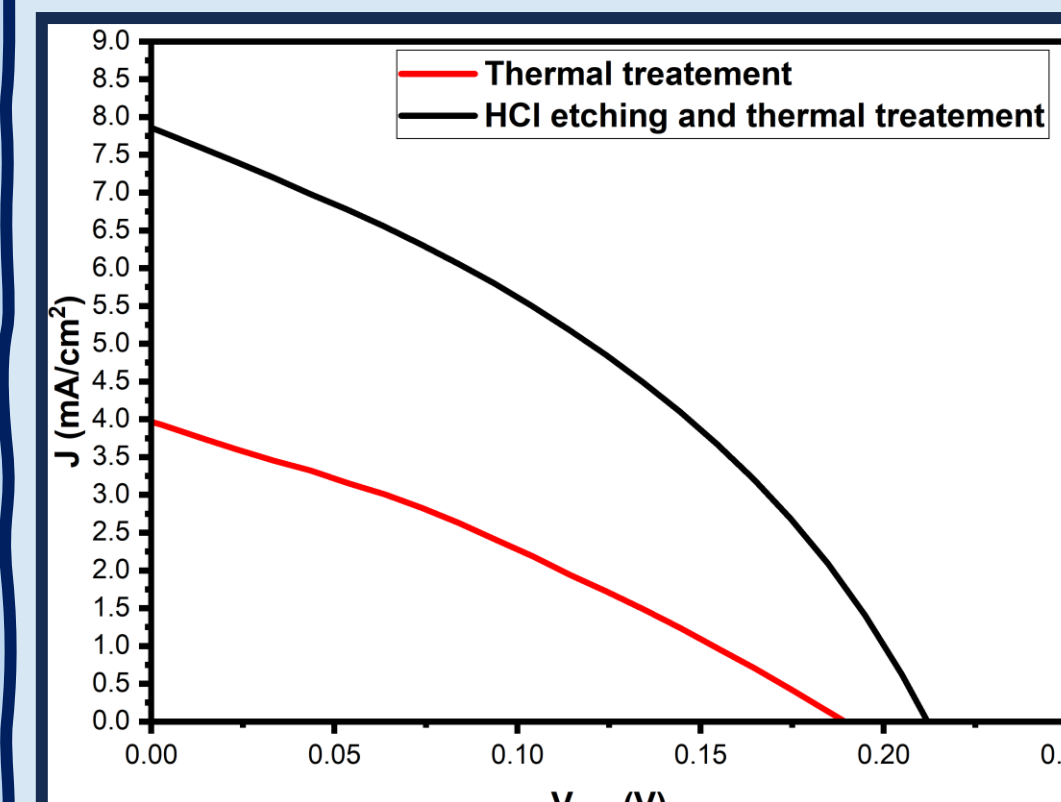


$J_{sc}=2.6$ mA/cm²
 $V_{oc}=61.9$ mV
FF=29.6%
Eff=0.05%

$J_{sc}=3.9$ mA/cm²
 $V_{oc}=192.3$ mV
FF=31.5%
Eff=0.24%

$J_{sc}=5.6$ mA/cm²
 $V_{oc}=276.5$ mV
FF=36.7%
Eff=0.57%

Thermal treatment and HCl etching:



$J_{sc}=3.9$ mA/cm²
 $V_{oc}=192.3$ mV
FF=31.5%
Eff=0.24%

$J_{sc}=7.85$ mA/cm²
 $V_{oc}=211.7$ mV
FF=36.3%
Eff=0.60%

- Ink** of metal salts and thiourea
- Blade coating** and **sol-gel transition**
- Annealing: **550°C** under **Argon**



Al
AZO
i-ZnO
CdS
CMTS
Mo
glass

