Wet-prepared thin films of Cu_2MnSnS_4: structural study and photovoltaic performances

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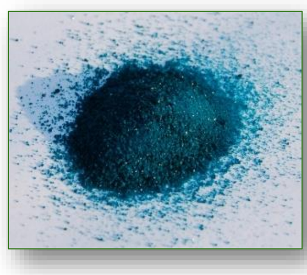
Cu_2MnSnS_4 (CMTS) is a promising candidate as low-cost and eco-friendly thin film absorber for photovoltaic (PV); nevertheless, reported efficiencies are still low, with a world record of 1.13% with CMTS made by sputtering and sulfurization [1].

In this work CMTS thin films were made by a low-cost method, starting from blade coating of a solution containing all the precursors followed by an annealing at 550°C under argon. CMTS thin films were extensively characterized by the means of grazing-incidence X-ray diffraction (GI-XRD) employing different incident angles probing different thin film depths.

All the samples characterized by GI-XRD exhibited stannite structure as expected for CMTS. The impact of composition of the starting solution and of post deposition was evaluated, finding an excellent agreement between GI-XRD data and PV performances. Combined effect of post deposition treatments and aging of the device gave the record efficiency for wet-synthesized CMTS [2].

[1] V. Trifiletti et al., Solar Energy Materials and Solar Cells 254, 2023, 112247 [2] F. Butrichi et al. Solar Energy Materials and Solar Cells 272, 2024, 112924

Preparation



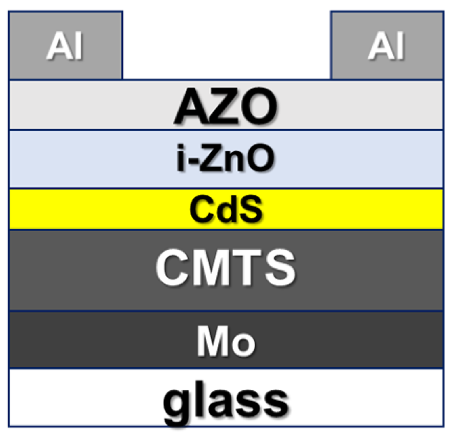
$Cu(CH_3COO)_2 \cdot H_2O$

$Mn(CH_3COO)_2 \cdot 4H_2O$

$SnCl_2 \cdot 2H_2O$

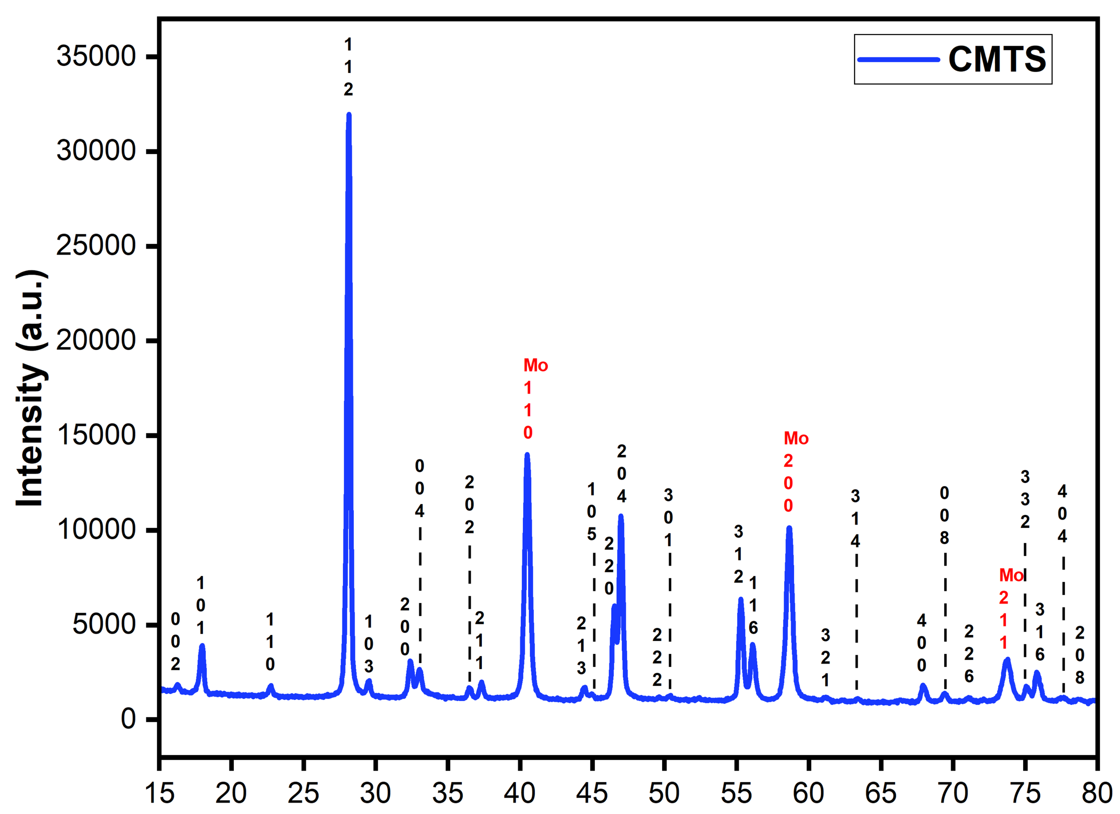
Thiourea

- **Solution preparation**: metal acetates and thiourea dissolved in dimethyl sulfoxide (DMSO) with potassium chloride as additive
- **Deposition:** blade-coating technique on molybdenum-coated soda-lime glass substrates
- **Annealing:** conducted at 550°C in an argon atmosphere without external sulfurizing agents



Structure identification

GI-XRD pattern of a CMTS thin film

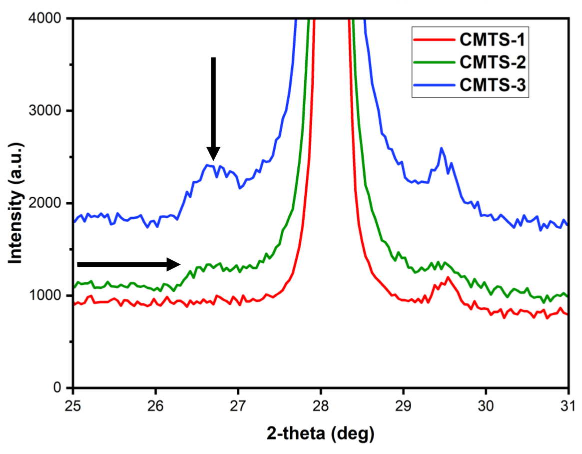


- all peaks can be assigned to the stannite structure with no hints of secondary phase
- Bragg peaks marked in red are due to the molybdenum substrate
- LeBail refinement was applied to determine lattice parameters and to analyse the thin film microstructure

Solution composition

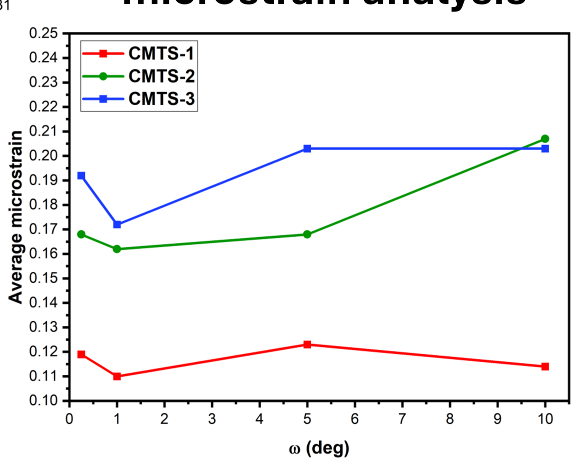
Composition	[Mn]/[Sn]	[Cu]/([Mn]+[Sn])
CMTS-1	1.00	0.89
CMTS-2	1.13	0.89
CMTS-3	1.27	0.89

GI-XRD pattern (part)



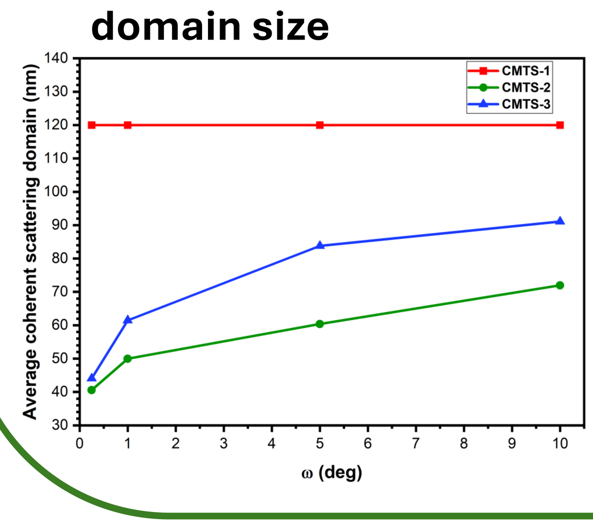
➢ CMTS-2 and CMTS-3 exhibit features typical of stacking faults

microstrain analysis



➢ CMTS-1 presents less microstrain respect to other compositions

coherent scattering domain size



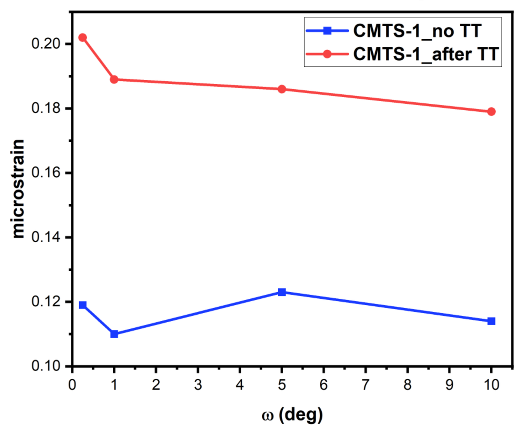
ω: incident angle of X-rays in GI-XRD experiment, correlates with investigated thin film depth

➢ CMTS-1 presents bigger coherent scattering domains

Thermal treatment

thermal treatment of the complete device at 260°C for 10 minutes on titanium hotplate

microstrain analysis

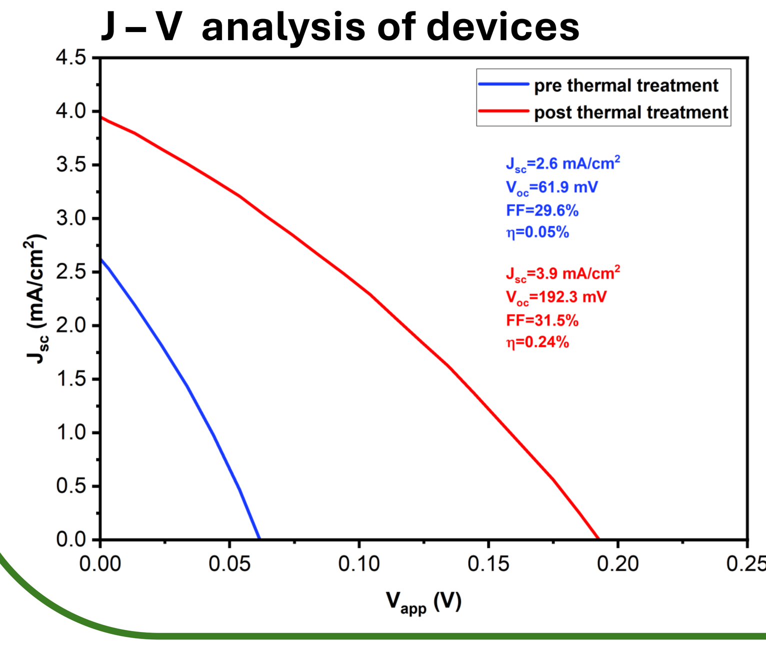


lattice parameter before and after thermal treatment

ω=10.00°		
CMTS-1	a=b (Å)	c (Å)
no TT	5.514	10.826
after TT	5.511	10.842

➢ elongation of the unit cell and increase in microstrain suggest cadmium interdiffusion from CdS used as buffer layer

J – V analysis of devices

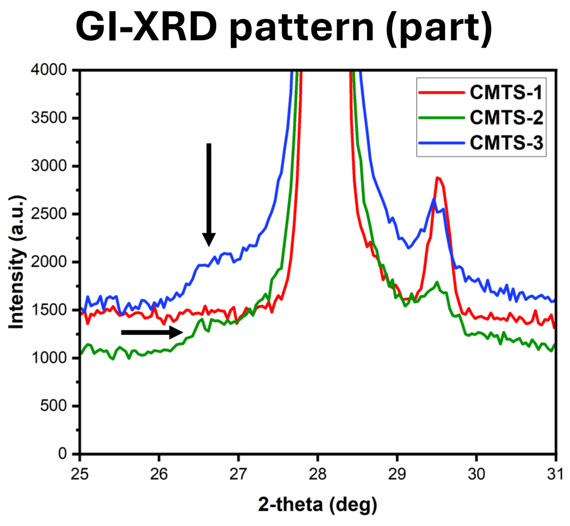


➢ improved PV parameters after thermal treatment

HCl etching

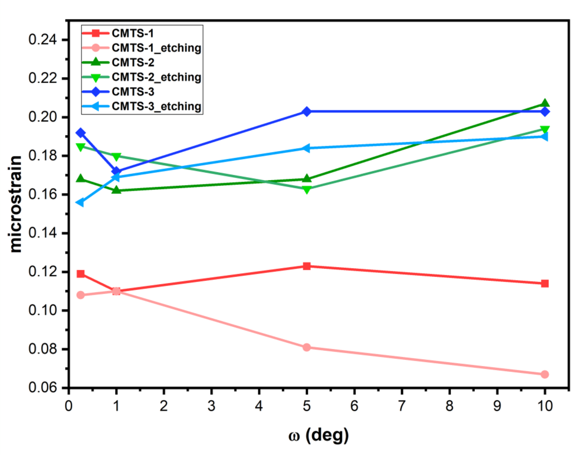
chemical etching of the absorber in a 3% HCl solution at 75°C for 10 minutes

GI-XRD pattern (part)

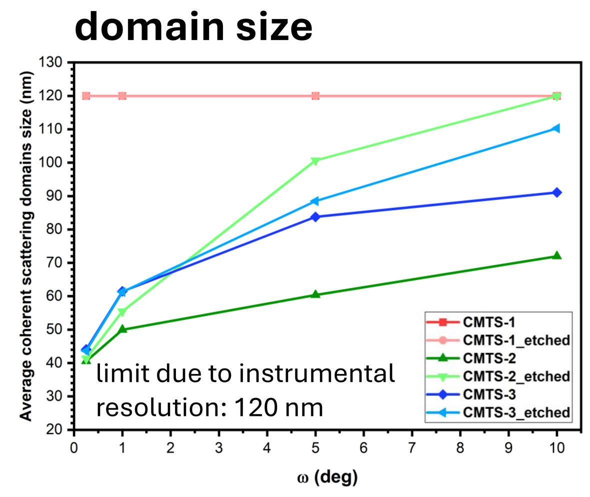


➢ stacking fault features are reduced in CMTS-2 and CMTS-3

microstrain analysis

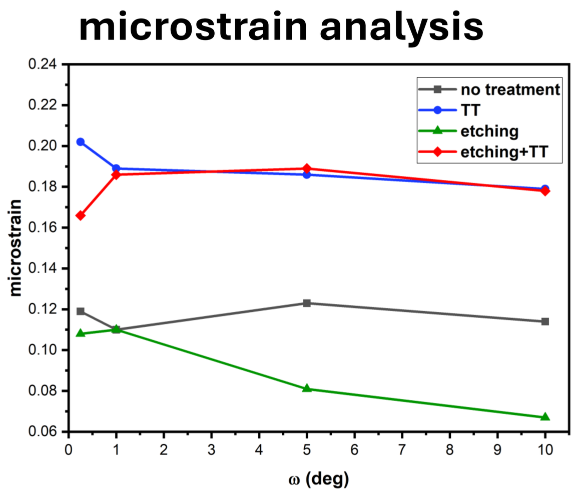


coherent scattering domain size

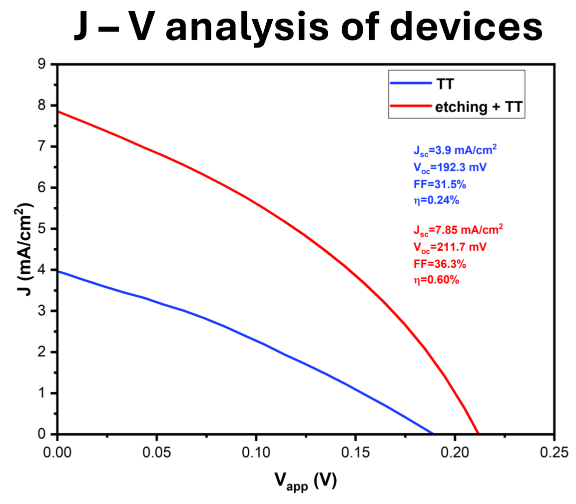


➢ chemical etching of the absorber has an improving impact on the thin film microstructure

microstrain analysis



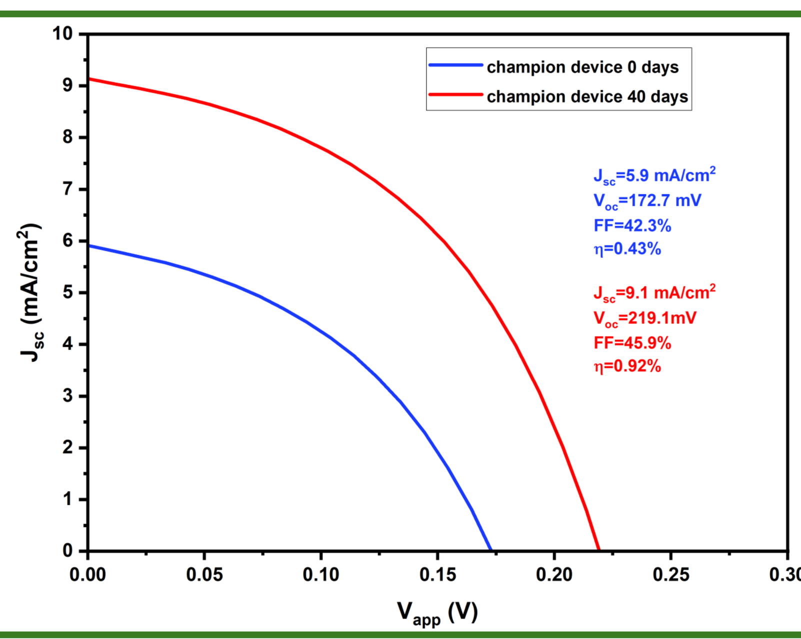
J – V analysis of devices



➢ combined effect of thermal treatment and etching results in an improvement in microstructure as well as in PV parameters

Aging

Complete device left in air at room temperature for 40 days



➢ aging of the device has a beneficial effect on PV performances

➢ combined effect of thermal treatment, HCl etching and aging of the device gave the record efficiency of η = 0.92%

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