

Investigations of quaternary phase diagram of Cu-Zn-Sn-S from thin films deposited by DC pulsed reactive magnetron sputtering

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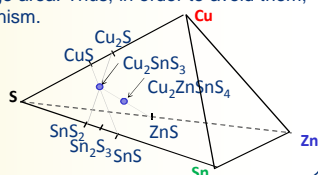
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Introduction

Cu₂ZnSnS₄ (CZTS) kesterite, composed of earth-abundant elements, is a good candidate for low cost and efficiency photovoltaic applications [1].

However, the instability of CZTS during the growth can cause the decomposition of this structure into binaries and ternaries. Hard process conditions could be a limiting factor for the manufacturing on a large area. Thus, in order to avoid them, it is important to study their formation mechanism.

In this view, thin films based on the quaternary phase diagram of Cu-Zn-Sn-S were deposited by DC pulsed reactive magnetron sputtering.



Conclusion

Cu_{2-x}S, Sn_xS_y, ZnS, Cu₂SnS₃ and CZTS thin films were deposited on glass and Mo/glass substrates using pulsed DC reactive magnetron co-sputtering from Cu, Zn and Sn targets.

We found that the cracker is the key for the growth of S-rich materials.

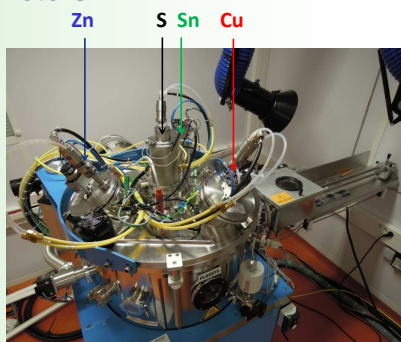
At high temperature, the losses of Zn, S and SnS are significant.

The deposition rate of Zn drops dramatically because of the target poisoning under sulphur atmosphere.

Solar cell based on CZTS with an efficiency of 1.2 % was achieved. The low efficiency was attributed to the presence of secondary phases Cu_{2-x}S and ZnS.

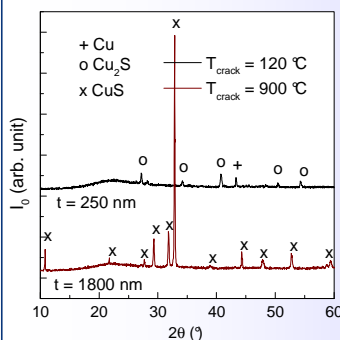
1/ Deposition parameters

- DC pulsed power supplies
- 3 targets : Cu, Zn and Sn
- S / Se cracking temperature
- S / Se sublimation temperature
- Deposition temperature
- Substrates : - Mo/Glass
- Glass
- Size : 5 X 5 cm²



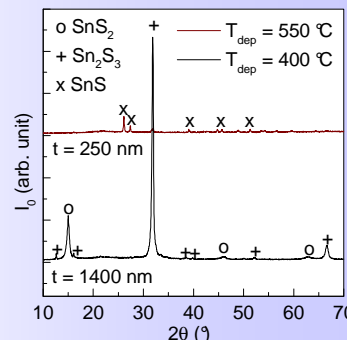
3/ Cu-S / glass

XRD

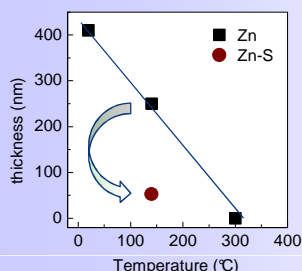


4/ Sn-S / glass

XRD

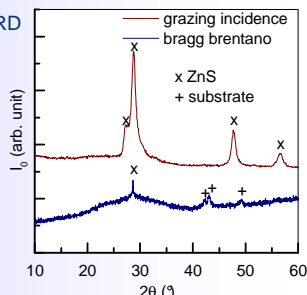


2/ ZnS / glass



- Strong volatility of Zn at HT
- target poisoning under S atmosphere

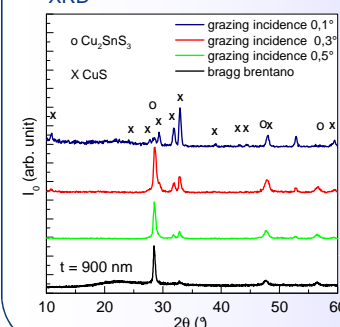
XRD



- ZnS is well crystallized
- XRR : t = 52 nm, r = 3.5 nm
- D = 4.3 g.cm⁻³ (D_{th} = 4.1 g.cm⁻³)

5/ Cu₂SnS₃ (CTS) / glass

XRD

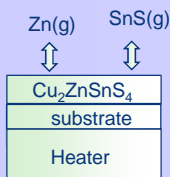


- Strong sulphur cracking at 900°C
- Growth of S-rich sulphide films
- Strong volatility of Sn-S at HT [2]
- Segregated layer of CuS on CTS [3]

5/ CZTS / Mo / glass

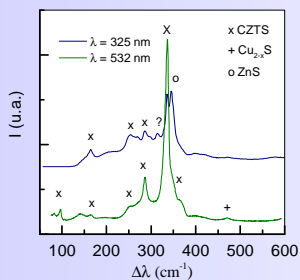
XRF

Ratio	T _{dep} (°C)	20	550
Cu / Sn		0.7	2.1
Cu / Zn		0.8	2



- Strong volatility of Zn and SnS during the deposition at HT

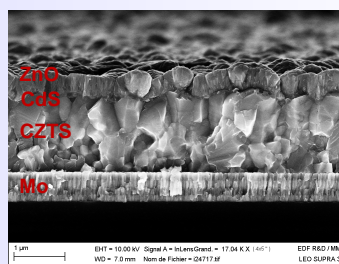
Raman spectroscopy



- CZTS is well crystallized
- Presence of Cu_{2-x}S and ZnS

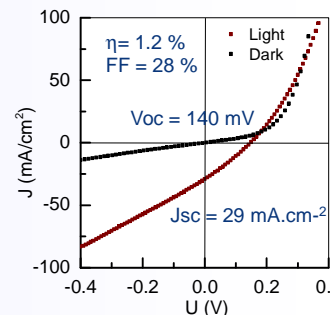
ZnO:Al / ZnO / CdS / CZTS / Mo / glass

MEB



- grains size of CZTS ~ 0.5 - 1 μm
- CdS / CZTS and CZTS / Mo are sharp

I-V measurement



- low efficiency can be attributed to the presence of Cu_{2-x}S and ZnS