Deposition of $CuInS_2$ by Atomic Layer Deposition as absorber for thin film solar cells

N. Schneider[1,2,3], P. Genevée[1,2,3], F. Donsanti[1,2,3], D. Lincot[1,2,3]

1- EDF R&D, Institut de Recherche et Développement sur l'Energie Photovoltaïque (IRDEP), 6 quai Watier, 78401 Chatou, France

2- CNRS, IRDEP, UMR 7174, 78401 Chatou, France

3- Chimie ParisTech, IRDEP, 75005 Paris, France

*E-mail: nathanaelle-externe.schneider@edf.fr , pascal-genevee@chimie-paristech.fr, frederique.donsanti@edf.fr,

Introduction

Atomic layer deposition (ALD) has gained a great interest in the recent years in the field of photovoltaic applications, in particular in CIGS based solar cells. So far, very few studies on the deposition of $CuInS_2$ (CIS) absorbers have been reported using this method[1].
The aim of this study is the investigation of the feasibility of preparing very thin layer of CIS by this method for making a complete solar cell by ALD.

- First, we tried to grow directly CIS films in a one-step process by alternating Cu_2S and In_2S_3 growth cycles.
- Secondly, we grew In_2S_3 on Cu_2S layer and achieved the deposition of homogeneous films with CIS stoechiometry.

[1]: M. Nanu, L. Reijnen, B. Meester, J. Schoonman, A. Goossens, $CuInS_2$ thin films deposited by ALD, *Chemical Vapor Deposition*, **10**, 45–49 (2004)

One step CIS deposition

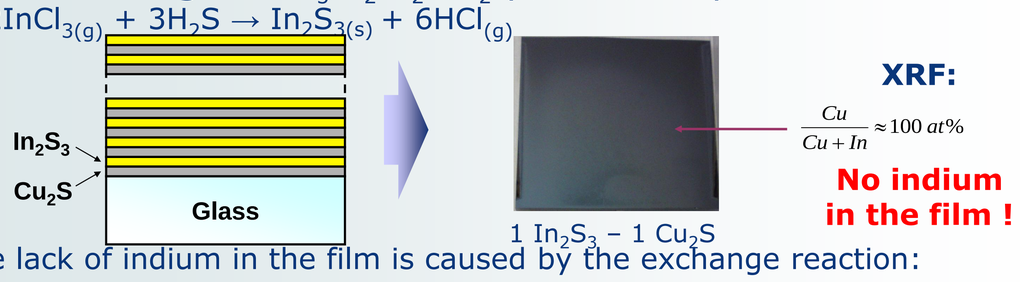
Films were grown in a Microchemistry F120 ALD reactor.

Temperatures:

Substrate: 425 - 500°C
Sources: T_{CuCl} = 380°C and T_{InCl3} = 345°C
Pressure: 5 mbar

$CuInS_2$ formation: $Cu_2S + In_2S_3 \rightarrow 2CuInS_2$

- **First stage**: $CuCl/N_2/H_2S/N_2$ (2/1.5/2/1.5 s)
  $2CuCl_{(g)} + H_2S \rightarrow Cu_2S_{(s)} + 2HCl_{(g)}$
- **Second stage:** $InCl_3/N_2/H_2S/N_2$ (2/1.5/2/1.5 s)
  $2InCl_{3(g)} + 3H_2S \rightarrow In_2S_{3(s)} + 6HCl_{(g)}$

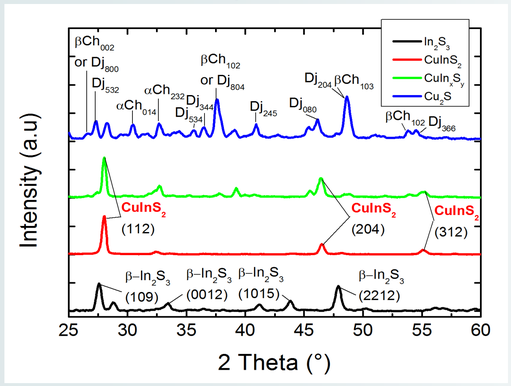


The lack of indium in the film is caused by the exchange reaction:

$In_2S_{3\ (s)} + 6\ CuCl_{\ (g)} \rightarrow 2\ InCl_{3\ (g)} + 3\ Cu_2S_{\ (s)}$ $\Delta G(500°C) = -94\ kJ.mol^{-1}$

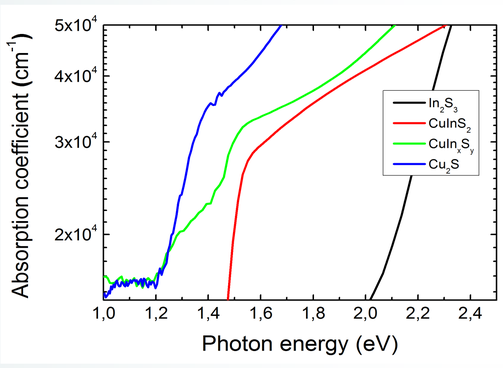
Films properties

XRD patterns



GIXRD patterns confirm the deposition of β-In_2S_3; $CuInS_2$; α-Cu_2S and β-Cu_2S

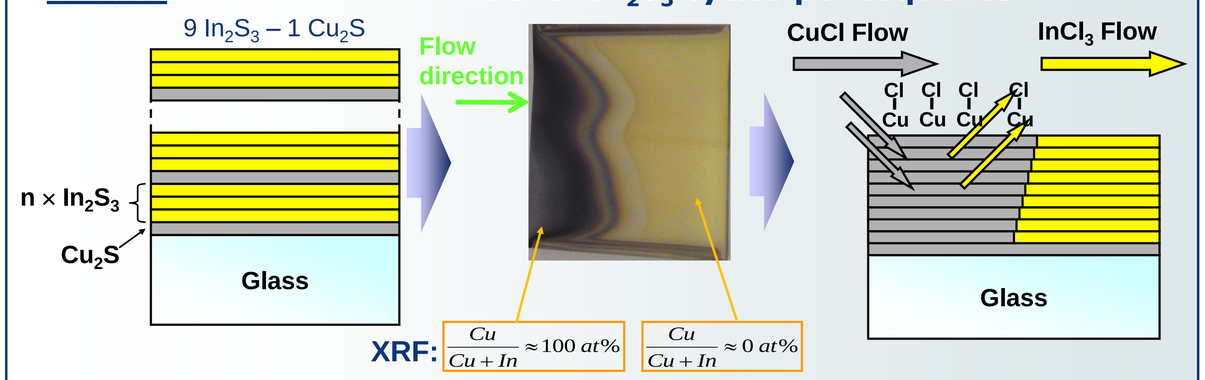
Optical properties



Bandgaps measured corresponding to: In_2S_3 (2.0 eV), Cu_2S (1.2 eV) and $CuInS_2$ (1.45 eV)

"In insertion into Cu_2S" CIS deposition

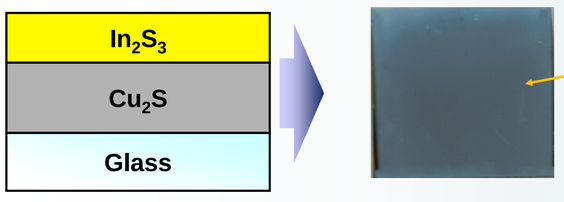
1st idea : increase the number of In_2S_3 cycles per sequence

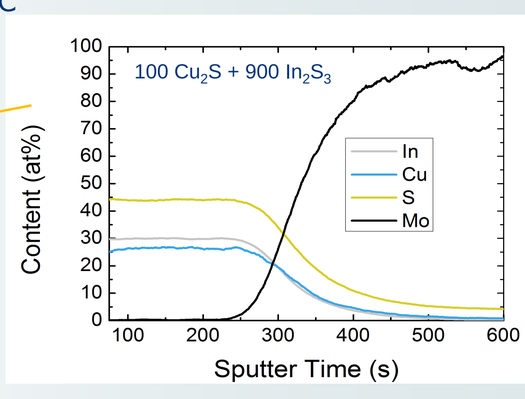


Competition between CuCl adsorption and the exchange reaction.
In this case, the exchange reaction is predominant.

Solution : use a two-step deposition process

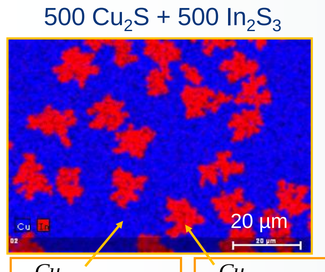
The In_2S_3 film is grown on a Cu_2S film to avoid the undesired exchange reactions.
Deposition temperature for both layers = 380°C



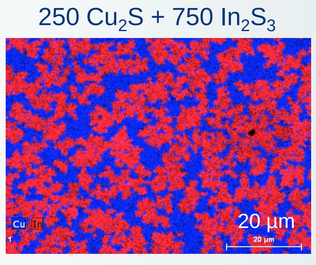


In some cases, the deposited films seem uniform but the EDS characterization show that indium is added in small islands forming directly $CuInS_2$ grains.

500 Cu_2S + 500 In_2S_3

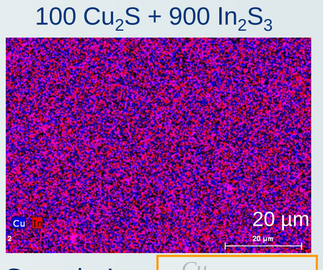


250 Cu_2S + 750 In_2S_3



Size of "CIS islands" increases

100 Cu_2S + 900 In_2S_3



Sample is **uniform**

$\frac{Cu}{Cu+In} \approx 55\ at\%$

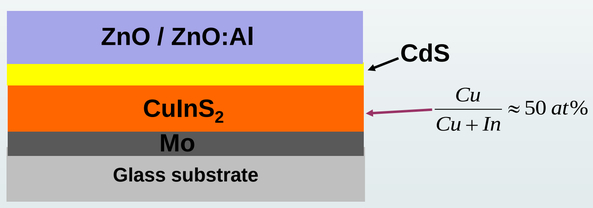
Conclusion

- ALD deposition of ultrathin CIS films was achieved at low T (<400°C)
- CIS used as absorber in solar cell : 2.8% of efficiency
- Improvement of the cell efficiency to be expected by:
  - Use of different precursors for indium and copper
  - Insertion of gallium and/or selenium into the film

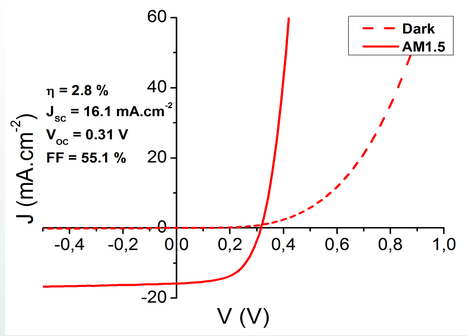
Optoelectronic results of ALD-CIS solar cells

Solar cells were completed with:

- CdS (Chemical Bath Deposition)
- ZnO/ZnO:Al (RF Magnetron Sputtering)



J-V characterization

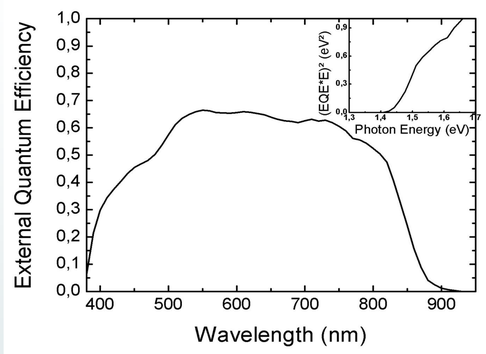


Efficiency of 2.8%

Good J_{SC} ➔ good light absorption despite the low film thickness (< 300 nm)

Small V_{OC} ➔ current collection losses?
➔ non-radiative recombination?
➔ low doping level?

External Quantum Efficiency



EQE quantum efficiency corresponding to a typical $CuInS_2$ solar cell

EQE limited to 0.7 by the low thickness of the absorber layer