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► To cite this version:

Eric Gautron, Thomas Lepetit, Sylvie Harel, Ludovic Arzel, Lionel Assmann, et al.. Heterointerfaces TEM characterization of buffer layers in KF treated CIGS solar cells. Towards a new buffer layer?. European Microscopy Congress, Aug 2016, Lyon, France. Wiley-VCH Verlag GmbH & Co. KGaA, 2016, 10.1002/9783527808465.emc2016.6618 . hal-02138680

HAL Id: hal-02138680

<https://hal.science/hal-02138680>

Submitted on 24 May 2019

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Heterointerfaces TEM characterization of buffer layers in KF treated CIGS solar cells. Towards a new buffer layer?

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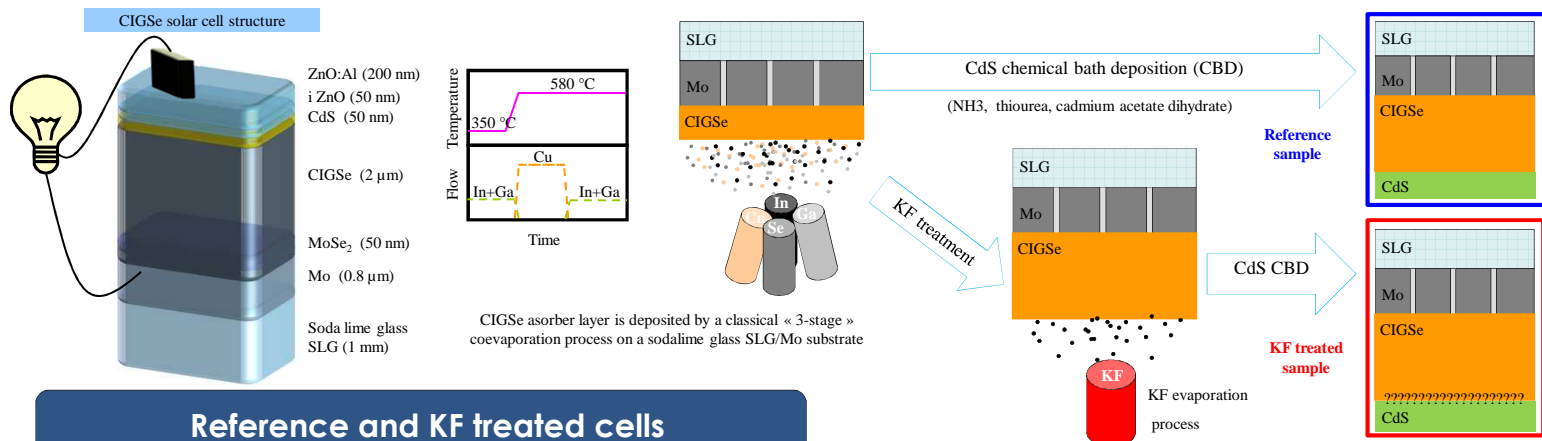
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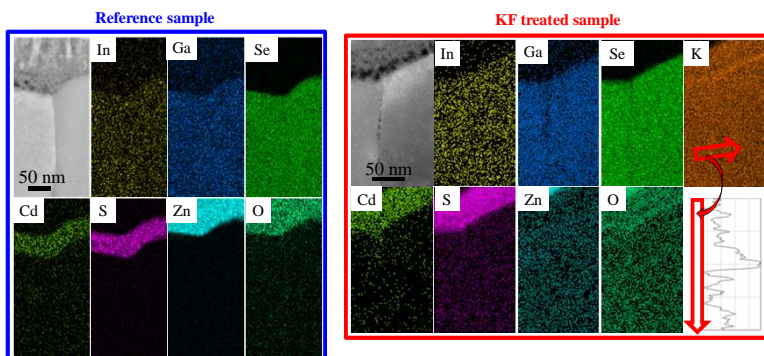
Photovoltaic performances of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) solar cells recently increased with the introduction of a KF treatment between the deposition stages of the CIGS (p-type semi-conductor) and the CdS (n-type SC) layers. We evidenced on our solar cells that KF treatment involves segregation (O and K) and depletion (Ga, Se, Cu) near the CIGS/CdS interface and the formation of an interface layer (mainly with Cd, In and S). Based on the composition of this layer, we proposed to replace the KF treatment and the CdS chemical bath deposition by a single stage of CdIn_2S_4 by physical vapor deposition.

CIGS solar cell growth with or w/o KF treatment



Reference and KF treated cells

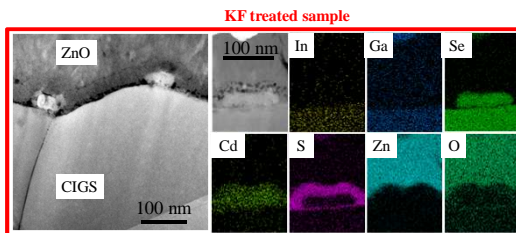
Cross section samples were prepared by FIB. Special attention was paid to limit artefacts due to ion beam.



EDX mapping of the KF treated sample revealed a depletion of Ga, Se, sometimes Cu and the presence of K at grain boundaries near the CIGS/CdS interface. K and O were detected at this interface. Such behavior was not observed for the reference sample.

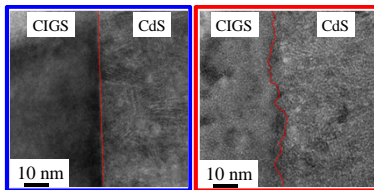
Few particles were observed in the buffer layer of the KF sample. They are made of CdSe and are covered by a CdS layer.

A thin layer containing Cd, In, S and O separates those CdSe particles from the CIGS layer.



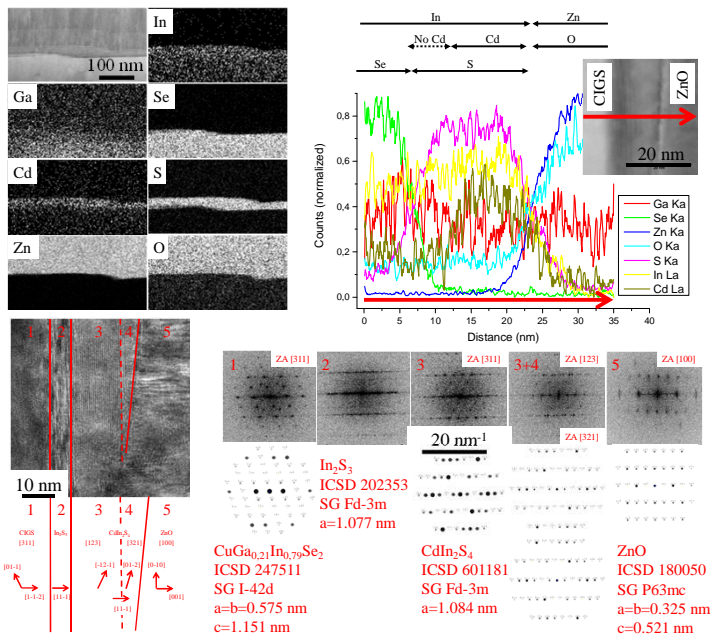
Segregation (O and K) or depletion of elements (Ga, Se and Cu) near interfaces (grain boundaries or CIGS/CdS interface), diffuse interface and formation of CdSe particles in the buffer layer could explain the better PV performances of the KF treated sample.

Such performance could also be due to a few nm thick layer composed mainly of Cd, In, S and O between CIGS and CdS (evidenced by EDX, XPS and EXAFS, not shown here).



CdIn_2S_4 as a new buffer layer ?

Based on the results obtained on the KF treated sample, an alternative buffer layer made of CdIn_2S_4 was synthesized by physical vapor deposition (PVD). PV characteristics were nearly as good as with a CdS buffer layer obtained by CBD.



An alternative buffer layer of CdIn_2S_4 was synthesized by PVD. It is made of a 5 nm thick interface layer made of In_2S_3 misaligned planes between CIGS and a well crystallized CdIn_2S_4 layer.

Such stacking is possible because the crystalline structures of CIGS along [112], In_2S_3 along [111] and CdIn_2S_4 along [111] are very similar.

Facilities used for this work :

FIB ZEISS NVision40, TEM JEOL 2010 and FEI Titan ETEM (CLYM, Lyon)

FIB FEI Helios Nanolab 450S, TEM FEI Themis ChemiSTEM (INL, Braga)

PIPS Gatan 691, TEM Hitachi HF 2000 (IMN, Nantes)

➤ **KF treatment involves depletion (Ga, Se, Cu) or segregation (O, K) near the CIGS/CdS interface, formation of CdSe particles and a diffuse interface. An interface layer composed mainly of Cd, In, S and O between CIGS and CdS was identified.**

➤ **A CdIn_2S_4 was proved to be a good candidate to replace the « classical » CBD CdS buffer layer. This allows a complete in-vacuum process which is critical for industry manufacturing.**

➤ **The next step of this work is to replace Cd by Zn to obtain a ZnIn_2S_4 buffer layer in order to produce solar cells without Cd (for health care consideration).**