ESRF	**Experiment title:** Spatially resolved composition and functionaliy of kesterite thin film solar cells	**Experiment number**: MA-3504
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Report:

It is the aim of this project to study the local composition and functionality of kesterite-based thin film solar cells by applying spatially resolved X-ray fluorescence (XRF) and X-ray beam induced current (XBIC) measurements on thin cross section lamellas. The results will provide original insight into lateral and depth-dependent compositional fluctuations of the absorber and will, in the future, help to reveal their impact on the solar cell performance.

Kesterite-based thin film solar cells were prepared by two different routes. In Dr. Edgardo Saucedo's group at the Catalonia Institute for Energy Research (IREC), Spain, $Cu_2ZnSnSe_4$ (CZTS) solar cells were grown by sputtering a Cu-Zn-Sn metallic precursor on a Mo-coated glass substrate. The precursor was subsequently selenized in a two-stage process to yield the kesterite absorber layer. The latter was then topped with a CdS buffer layer and a ZnO/In_2O_3-SnO_2 (ITO) window layer [1]. In Dr. Gerardo Larramona's group at IMRA Europe S.A.S., France, $Cu_2ZnSn(Se,S)_4$ absorbers were prepared on Mo-coated glass substrates by spray coating a water-ethanol-based ink containing small Cu-Zn-Sn-S colloids. This precursor was then transformed into the kesterite absorber layer in a two-step annealing process facilitating both grain gowth and subsequent selenization [2]. A stoichiometric, homogeneous, single-phase $Cu_2ZnSnSe_4$ powder sample synthesized by solid state reaction of the pure elements in Prof. Dr. Susan Schorr's group at the Helmholtz Center Berlin for Materials and Energy was used as calibration sample [3].

To achieve high spatial resolution and to minimize averaging along the beam direction, thin cross section lamellas were prepared out of the samples using a focused ion beam system [4]. The thickness of the lamellas was between 170 and 340 nm, which represents a good compromise between mechanical stability and count rate on the one hand and minimal

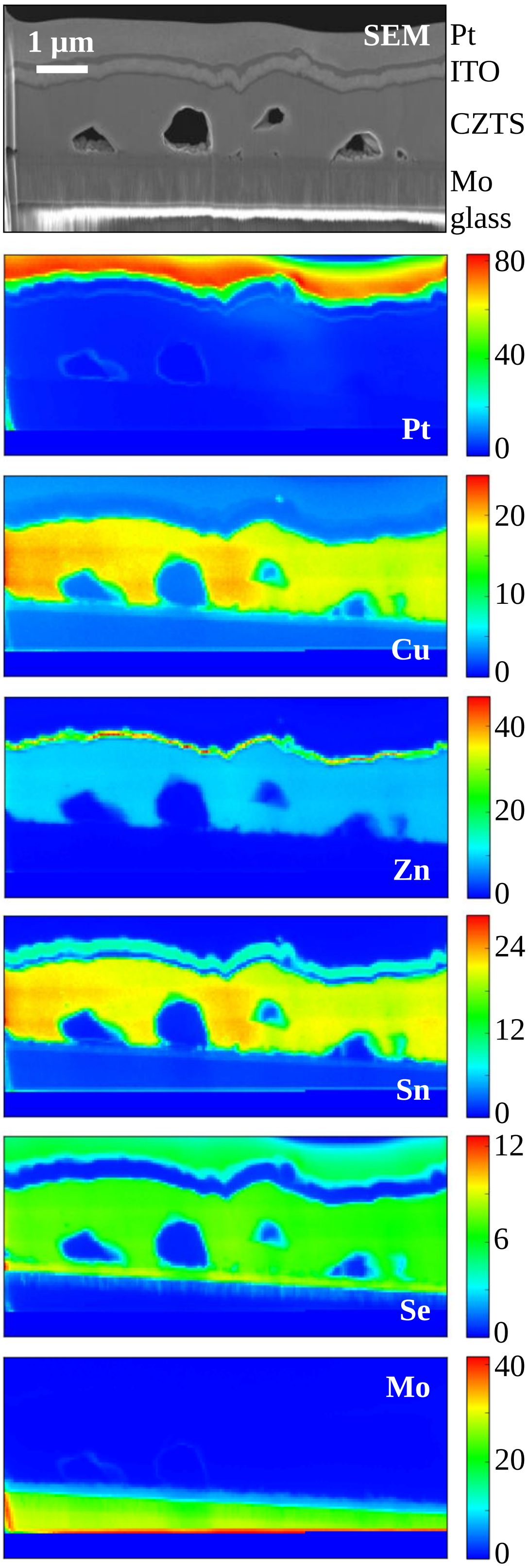

Figure 1: *Scanning electron micrograph (SEM) and elemental XRF intensity maps (scale bar: 10^3 counts) for a cross section lamella of an ITO/ZnO/CZTS/Mo/glass solar cell with a Pt protective layer.*

averaging on the other hand. Two to three lamellas were prepared for each of the samples.

Spatially-resolved XRF measurements were performed at station ID16B-NA in pink beam operation mode using an energy of 29.6 keV. This allows the excitation of the fluorescence K-lines for all elements of interest (ranging from Cu to Sn), which significantly improves the quantification of the local sample compositions. The beam spot size was 51 x 54 nm^2 and the fluorescence radiation was detected with two 3-element Si drift detectors. A multilayer standard from AXO and a thin cross section lamella of the stoichiometric CZTS reference sample were measured repeatedly throughout the beamtime to calibrate the measurements and to check the stability of the setup.

For each preparation method, three different nominal compositions of the CZTS absorber were prepared and two different lamellas were measured for each, corresponding to a total of 12 lamellas. An example is shown in Figure 1, where the Pt protective layer, the ITO and ZnO window layers, the CZTS absorber and the Mo back contact are all clearly apparent in the respective elemental XRF intensity maps. A detailed analysis of all samples measured is currently under way using the software PyMca. The results will provide a comprehensive picture about the lateral and depth-dependent fluctions in the local kesterite composition as a function of the integral absorber composition and the thin film preparation process.

Additionally, first tests of simultaneous XRF and XBIC measurements of thin film solar cells were conducted in plan-view geometry. In particular, the use of a special sample holder that allows the contacting of the samples at the home institution prior to the beamtime and the detector settings suitable for measuring photovoltaic material were investigated. Successful XRF and XBIC measurements were thus achieved for three different solar cells. Furthermore, possible improvements of the setup were identified, which will be implemented in the framework of our upcoming Long Term Proposal MA-3564.

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[3] L. E. Valle Rios, K. Neldner, G. Gurieva, S. Schorr, J. Alloys Comp. 657, 408 (2016).
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