Nowadays, the best efficiencies of Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) solar cells are obtained from absorber layers that have been fabricated using sequential processes, including the deposition of metallic stack precursors typically by sputtering technique and followed by the reactive annealing under chalcogen atmosphere. The sputtering deposition is a widely known technique for the easy growth of metallic layers, although the deposition rates, the growth morphology and nucleation, or the roughness in some cases can be an issue in the following steps, leading to inhomogeneities in the final layers after the thermal annealing. Nevertheless, MBE (molecular beam epitaxy) technique can have some advantages to obtain very high quality metallic layers, with an accurate control of the growth due to the ultra high vacuum conditions ($p < 10^{-8}$ Torr) as well as very high purity. In this work, we study the use of advanced MBE systems to grow metallic stack precursors, alternatively to the sputtering [1] or the conventional thermal evaporation techniques [2], in combination with the commonly used conventional tubular furnace selenization in order to obtain high quality Ge-doped CZTSe absorbers. To perform this research, we deposit Cu/Sn/Cu/Zn/Ge metallic stack precursors by MBE technique, which are subjected to the selenization process using conventional tubular furnaces. Afterward, standard CdS buffer layers and $i$-ZnO + ITO window layers are deposited in order to complete the devices. After the initial investigations and optimizations, we achieved a 9.2% efficiency CZTSe:Ge solar cell (see JV characteristics in Figure 1), which is a reasonable efficiency considering the high degree of overselenization observed in the Mo back contact (excessive MoSe$_2$ formation). The presence of such a thick layer of MoSe$_2$ is expected to have undesired consequences in the solar cell devices like increased series resistance, limiting their performance. In fact, this points out the importance to optimize the thermal annealing step when the metallic precursors properties are changed due to the their growth conditions. A detailed characterization of the MBE-deposited layers and the produced kesterite absorbers will be presented, using SEM, EDX, EPMA, XRF and Raman spectroscopy characterization tools. For the solar cell analysis and characterization, JV curves and EQE will be presented. Also, the impact on the devices of the thick MoSe$_2$ layers observed at the Mo/CZTSe:Ge interface will be discussed and compared with absorbers produced by other physical vapor deposition techniques such as sputtering [1] and co-evaporation [2].

Figure 1: JV curve and parameters of the best performing solar cell

References