

In-situ Process Monitoring for Chalcopyrite Thin Films

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The growth of polycrystalline CuInSe_2 and CuInS_2 thin films for solar cells can be accomplished by the principal path ways (1) post-chalcogenisation of metallic precursors layers and (2) simultaneous deposition of metals and chalcogen. In order to learn more about the mechanisms and the reaction kinetics, in situ investigations have been performed using bulk sensitive (XRD) and surface sensitive in situ methods. Simultaneously, the processes have been monitored by laser light scattering (LLS). The latter is a simple and fast technique which is apt for process control even in production [1].

Energy dispersive X-ray diffraction (EDXRD) and LLS experiments have been conducted at the Hasylab (DESY). With a time resolution of 15 s, EDXRD is able to resolve phase transitions which occur during the sulfurization of metallic Cu/In layers. *Fig. 1* gives a series of EDXRD spectra recorded during the sulfurization of the metallic precursor. The graphs depict the time evolution of several peaks during a sulfurization experiments (bottom trace represents the ramp-up start). Clearly, the evolution of the CuInS_2 (112) diffraction is visible. This diffraction occurs already in the ramp-up period of the substrate and comes along with a strong decrease of the LLS intensity.

The area of the diffraction peaks is determined for each spectrum in *Fig. 1* and is plotted as a function of time in *Fig. 2*. The graph also contains the substrate temperature during the course of the sulfurization process. Due to the penetration depth of X-rays in the investigated wavelength range, the area of the diffraction peaks can, in a first appro-

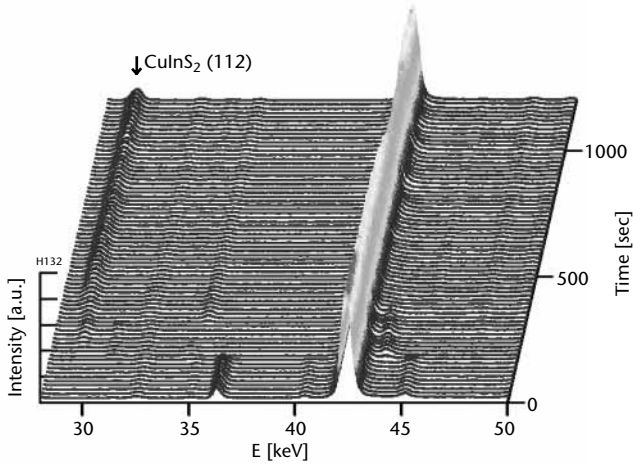


Figure 1:
Time series of EDXRD spectra during the sulfurization of a Cu-rich CuIn precursor on a molybdenum coated soda lime glass, 5 min heat up time, $T_{sub} = 500^{\circ}\text{C}$

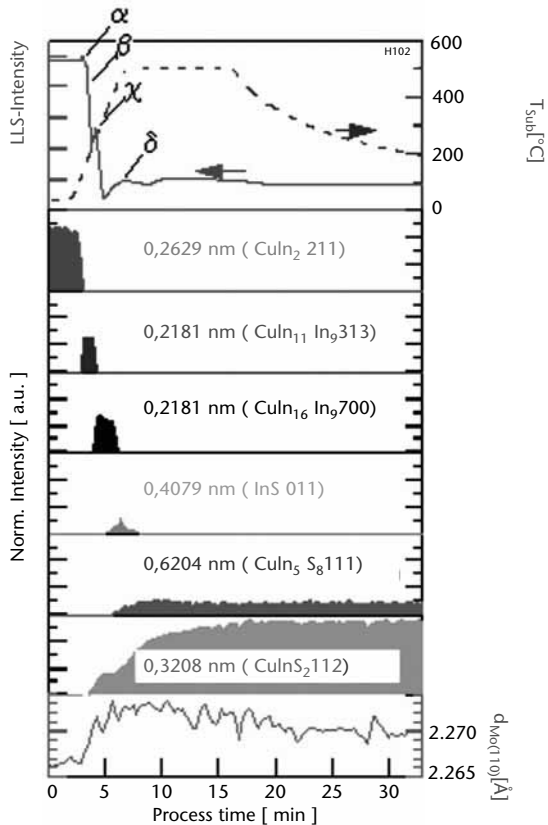
ximation, be considered as an indicator of a phase's volume fraction. From Fig. 2 a variety of phase transitions can be appreciated. These are intermetallic transitions and metal-semiconductor transitions. In addition, the position of the EDXRD peaks can be used to determine stress development in the layers. Fig. 2 gives the example of the Mo (110) lattice spacing as a function of time.

The combination of both optical and structural techniques has allowed the assignment of the following laser light transient features. The assignments, derived from Fig. 2, were:

- α : $\text{CuIn}_2 \rightarrow \text{Cu}_{11}\text{In}_9$
- β : surfacial CuInS_2
- χ : $\text{Cu}_{11}\text{In}_9 \rightarrow \text{Cu}_{16}\text{In}_9$

These assignments are very useful for the application of the LLS method for process control and were the basis for a patent application for an optically controlled chalcogenization process. We prepared solar cells from CuInS_2 films formed in the in-situ EDXRD chamber. Since they exhibited up to 10.6% efficiency, the relevance of these model experiments is demonstrated.

Figure 2:
(top) Temperature profile and LLS intensity, (middle) intensity of characteristic diffraction peaks and (bottom) EDXRD lattice spacings of Mo from the annealing of a Cu,In precursor ($\text{Cu/In} = 0.7$) on Mo/glass. Phases identified are given in parenthesis. Details of the process are 5 min heating-up, 10 min hold, and passive cooling. The d-spacing of the Mo 110 peak reveals stress release in the ramp-up period.



Literature

- [1] Ch. Pietzker, E. Rudigier, D. Bräunig, and R. Scheer, in 17th European Photovoltaic Solar Energy Conference; Vol. II, edited by B. McNelis, W. Palz, H.A. Ossenbrink, and P. Helm (WIP, Munich, Munich, 2001), p. 1031.