Experimental Report ME-562

In-situ investigation of the selenisation process
of metallic precursors for CuInSe$_2$ solar cells

This experiment was a continuation of ME-277 with an extended choice of the chemical composition of the samples and a higher temperature resolution of the data.

The aim was to clarify further the reaction mechanism for the crystallisation of the thin film solar cell material CuIn(Ga)Se$_2$ when grown from thin films under technologically relevant conditions by rapid thermal annealing. A reaction chamber (fig. 1) was used with an independently controllable sample and selenium source heating and adjustable vacuum pressure up to a base pressure of 1 mPa. This sample surrounding was fixed onto a two-circle-goniometer with an additional z-translation on beamline ID 15B. The incident beam was limited to a height of 40 µm and 300 µm width. It entered into the chamber through an 75 µm Kapton window, hit the sample (sample dimensions: 10 mm × 10 mm × 2 µm, deposited on 2 mm thick glass substrate) parallel to its surface where scattering appeared from the surface under the Bragg-reflection angles. The scattering volume of the samples can be estimated to be 1 mm × 300 µm × 2 µm = $0.6 \cdot 10^{-3}$ mm^3 from the beam dimensions and the penetration depth of the radiation used. Since the energy of the incident beam was 81 keV ($\lambda = 15$ pm) the penetration depth can be estimated to be 1 mm (1/e-decay) for an incident beam hitting the sample under 0°. If this angle of incidence deviated from zero the Debye-Scherrer ring pattern would loose its maximal resolution, since in this case the scattered intensity would originate from the whole length of the thin film sample.

The beam exit Kapton window was large enough to allow the almost 360° of the ring pattern to leave the reaction chamber and to be recorded by an image intensifier area detector with a readout time of 8 s. Together with 2 s illumination time and a constant heating rate of 0,5 K/s this resulted in a temperature resolution of 5 K per measured powder diagram.
The layer sequence of the samples was as follows:

Fig. 1:

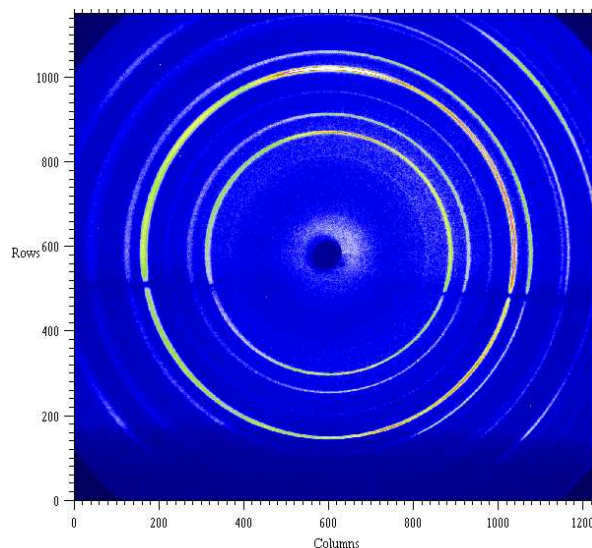View through the reaction chamber containing the sample fixed underneath the glowing heating rod.

Fig. 2:

Powder pattern obtained at 550°C in 2 s.
Thin film structure: Mo / Na / Cu / In / Se

2 mm thick glass substrates were coated with a barrier layer that prevents sodium ions to diffuse out of the glass into the molybdenum layer sitting above later serving as back electrode for the ready-processed solar cells. However, since it is known that a certain concentration of sodium

ions promotes the crystallisation of the semiconductor $CuInSe_2$, a sodium compound was deposited on top of the molybdenum layer in one half of the samples to study its influence on the chemical reactions of the precursor layer. Concerning this aspect we expect a temperature shift rather than new phases present during the heating process.

On top of the back electrode the samples contained a metallic layer of copper, indium and partly gallium which forms intermetallic phases already during its deposition process. Finally, most of the samples were evaporated with selenium as reactant for the metallic layer below. The thickness of this selenium layer was varied as well, to offer different amounts of excess of selenium referring to the stoichiometrically demanded portion.

Since all occurring compounds in the reaction process of these precursors are solid state except selenium which melts at 220°C the chemical reactions taking place in the samples can be studied with in-situ x-ray diffraction.

The samples were processed in a temperature range running from 30°C up to 550°C, whereby the formation of the $CuInSe_2$ semiconductor already occurs close to 375°C. At higher temperatures the chemical processes have come to an end and ordering of the initially defect chalcopyrite structure of $CuInSe_2$ takes place.

Since the ternary system Cu-In-Se has a quite complex phase diagram field, samples of the binary elemental systems Cu-Se and In-Se were investigated as well for the sake of a later calibration of our measured temperatures of phase transitions to the phase borders shown in the well-known binary phase diagrams.

Furthermore we investigated the phase sequence during rapid thermal annealing of the pure ternary system Cu-In-Se.

In industrially made solar cell materials not only copper, indium and selenium are present, but also gallium which partially substitutes the indium. Therefor, we also studied samples containing the pure metallic system Cu-Ga-In, but also Cu-Ga-Se for comparison with the ternary Cu-In-Se-system.

Finally we studied the quarternary system Cu-Ga-In-Se, which represents the technologically relevant process for the production of solar modules best.

The thermal annealing of a total of 33 different samples (leading to approximately 130 powder diagrams per each sample) was investigated during the 15 shifts of beam time and are currently analysed by qualitative phase analysis. The results will be compared to our earlier measurements [1, 2] of the formation of $CuInSe_2$ on the beamline ID 15B. As a byproduct of these measurements undertaken for phase analysis, textures and textural changes of the materials as well as enhanced grain growth can be studied as a function of temperature. These factors may also influence the efficiency of the grown absorber materials.

During selenisation, the back electrode material of the precursors is partly reacted to $MoSe_2$, which has favourable influence on the electrical properties of the solar module but may be detrimental for the mechanical properties depending on the preferred growth orientation. The growth and build up of preferred orientation of the $MoSe_2$ layer can be followed in the two-dimensional diffraction data as well.

References

[1] ESRF Experimental Report ME-277,
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[2] A. Brummer, V. Honkimäki, P. Berwian, V. Probst, J. Palm, R. Hock
    "Formation of Copper Indium Diselenide by the Annealing Of Stacked Elemental Layers –
    Analysis by In-situ High Energy Powder Diffraction', Thin Sol. Films 437, 297 – 307, 2003