For the in situ experiments on $CuInSe_2$ precursor stacks under processing conditions the high energy beamline ID15B was used in the powder diffraction mode. The primary x-ray beam had an energy of 81.85keV and a wavelength of 0.1515Å. The x-ray beam size at the sample position was controlled by a primary collimator made of tungsten slits to 70µmx300µm height and widths. The beam traverses the sample under zero degree incidence within the film plane and is scattered in a sample volume of $2\mu m \times 0.3mm \times 8mm = 4.8 \times 10^{-3} mm^3$. Half of the diffracted Debye-Scherrer ring system was detected in transmission with an image plate detector (MAR 345) in a distance of 61.5cm from the sample position. Exposure times for a powder diagram were 20s. With an heating rate of 25°C/min each image corresponds to a temperature range of 8.3°C. To decrease the readout time to 40s, the detection surface of the image plate was limited two half the active size. Powder diagrams were collected every minute. The detected q-range was $q \leq 0.46 Å^{-1}$. The resolution in this set up was governed by the sample geometry and the beam divergence. The precursor stack scatters over a length of 8mm into the Debye-Scherrer ring. Scattering angles at 81.85keV are small and were in the range $0° < 2\Theta < 8°$ for the set up chosen. The scattering volume is seen under these angles and the effective width of the scattered beam is 0.35mm at 2.5° 2Θ. This corresponds to a width of 0.02° in the central region of the collected powder diagrams due to the sample geometry only. Convoluted with the beam divergence this resulted in a experimental angular width of the Debye-Scherrer rings of 0.06° 2Θ. A two circle goniometer with a z-translation stage serves as an adjustable support for the sample environment. The z-translation has a precision of 0.2 µm, necessary to bring the thin film of average thickness 2µm (Mo + CIS) in scattering position. The diffraction set up was calibrated with iron powder to correct the data for the tilt of the detector towards the incident beam, determine the distance detector to sample and to calibrate the wavelength by the known lattice parameter of the standard sample.

The samples were clamped with their glass side in direct contact onto a resistive heater element mounted in a vacuum chamber. The steel chamber has two windows made of Kapton foil of 75µm thickness serving as an entrance for the primary x-ray beam and exit for the scattered radiation. Next to the sample a thermocouple (PT100) measures the temperature. To lessen the evaporation of Se and keep losses small, the precursors were covered by a second glass slide of thickness 0.1mm. The complete sample therefore was a stack of glass-metal/selenium-glass. The heater element was connected to a Eurotherm controller to ramp the sample temperature. Samples were heated with a rate of 25 $°C min^{-1}$ up to 550°C. The sample chamber was mounted on the two circle goniometer. The thin film was brought into the centre of the x-ray beam with the z-translation stage and adjusted parallel to the incident beam.

Phases and phase transitions in thin films of three binary systems, Cu-Se, In-Se, Cu-In and the ternary and quaternary systems Cu-In-Se-(Ga) were then investigated in a temperature range from 25°C to 550°C. Results for the binary systems can be compared to the known equilibrium phase diagrams of Cu-In, Cu-Se and In-Se. Cu-In and Cu-Se follow above 225°C the expectations based on the equilibrium phase diagrams. For In-Se deviations from the equilibrium diagram are observed over the entire temperature range investigated. The results on binary systems yielded the basis for the qualitative phase analysis of the phase sequences observed in CIS precursor stacks during thermal anneal. On the ternary and quaternary systems Cu-In-Se-(Ga) the reaction path up to the formation of CIS could be determined in real time and under process conditions. Deviations of phase sequences as expected from the equilibrium phase diagrams are attributed to chemical rather than thermal disequilibrium. CIS finally crystallises from the direct precursors $Cu_{2(-x)}Se$ and InSe within a melt rich in selenium. Figures 1 and 2 show part of the phase sequences observed in the systems Cu-Se and Cu-In-Se.

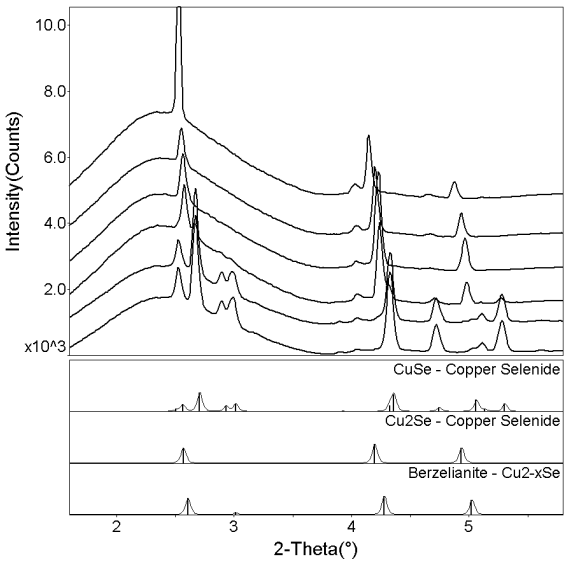

Fig. 1:
Transition of CuSe over $Cu_{2-x}Se$ into Cu_2Se at temperatures from 325°C – 550°C in the Cu-Se binary system.

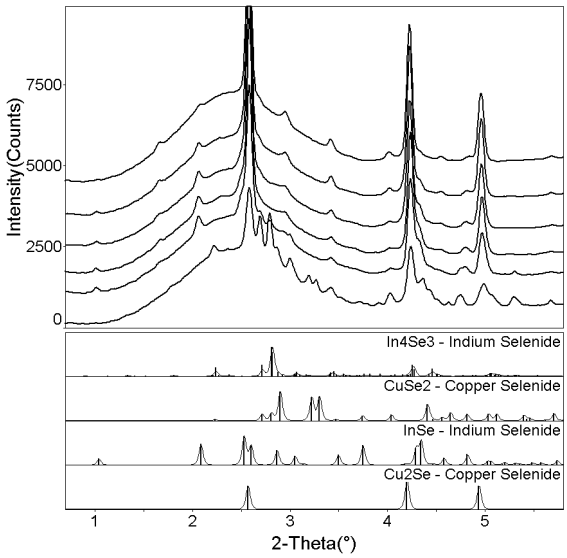

Fig. 2:
Final reaction stages towards CIS in the Cu-In-Se ternary system. CIS forms from the direct precursor phases $Cu_{2-x}Se$ and InSe within a selenium rich melt.

The Debye-Scherrer method employed proved to be excellently suited for the study of the CIS formation in a thermal annealing process under direct selenisation. Not only the phases and sequence of phase transformations can be observed under process conditions and 'real time' phase standards could be measured, but as well changes in texture of thin films and the onset of exaggerated grain growth in late stages of the $Cu_{2-x}Se$ and absorber formation can be observed. The information is measured on a representative sample volume. Due to an unexpected rescheduling on ID15B a fast CCD detector was not available at the time of the experiment. Thus an image plate was used and the time resolution achieved naturally was less than proposed. In a future experiment we want to achieve now a time resolution of a few seconds per diffractogram with a CCD detector. From the previous experiment we know, that especially a phase transformation at about 375°C leading to CIS from the precursors $Cu_{2-x}Se$ and InSe is rapidly progressing and needs a faster detector response.

The experiment laid a sound basis for further investigations of CIS formation by the rapid thermal annealing process as a function of process parameters like temperature profiles and selenium flow.