Photoelectron Spectromicroscopy at Chalcopyrite films
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In memoriam to Gertrude F. Rempfer on the occasion of her 100th birthday and her pioneering work on photoelectron microscopy

Abstract
CuInSe$_2$ films were prepared by MBE on GaAs (111)A substrates. ZnSe and ZnO are subsequently deposited in situ by MOMBE. Interface parameters like band offsets and morphology are studied by X-ray photoelectron spectroscopy (XPS) and Low energy electron diffraction (LEED). Spectroscopic XPEEM (X-ray Photo electron emission microscopy) at the U49/2 PGM2 beamline at BESSY was used to investigate the lateral homogenity of the interface. After annealing in situ a lateral inhomogenous In diffusion is observed into the ZnSe/ZnO interface.

Introduction
Chalcopyrite (CIS) thin film solar cells are the most efficient polycrystalline devices reported so far. Efficiencies on laboratory cells are reaching 20% /5/. In principle the devices are rather simple: the absorber is deposited on a Mo back contact and the contact to the ZnO window layer is achieved by a Cds buffer layer. ZnSe was proposed as an alternative buffer layer to omit the environmentally hazardous CdS. Recently the band alignment in CuInSe$_2$ (112) and (100) interfaces has been studied in detail by photoelectron spectroscopy /3/. Most studies on CIS materials are performed on technologically prepared interfaces /4/ here we report on well defined single crystalline samples grown by MBE (PRB). Lateral inhomogenities in the interface are influencing the performance of a solar cell device as recombination centers may be introduced in the band gap in the interface region. In PEEM interfaces and surfaces of materials can be investigated in a non-destructive way. PEEM has been introduced first in 1934 by Brüche /2/ and in the 60’s the pioneering work of Gert Rempfer /1/ established PEEM as a high resolution electron microscopy.

Experimental
CuInSe\textsubscript{2} were prepared by MBE on GaAs substrates and it was shown in angular resolved photoemission and LEED that they exhibit the chalcopyrite structure /6/. Samples were prepared in an all UHV integrated deposition and analysis system. ZnO is deposited in a dedicated MOMBE system (SiC-ZnO pap) from diethyl-zinc (DEZ) and water. After characterization by XPS and LEED samples were transferred by an transportable UHV chamber to the U49/2-PGM2 beamline at BESSY and introduced in the ELMITEC XPEEM3 equipped with an hemispheric electron spectrometer to filter the kinetic energies of the PEEM images (imaging analyzer). Fig 1 shows as an example of the operation mode. Images of an Ag film deposited on Si (111) are taken after annealing to 700°C. The images are taken at the Si2p level and the Ag 3d emission respectively by choosing the appropriate photon energy with fixed kinetic energy.

![Fig1 Energy filtered XPEEM images of an Ag island film on Si(111) left image taken at the Si2p binding energy, right at the Ag 3d binding energy. Field of view 10µm, resolution 30nm for Si2p image as determined from the edge jump.](image)

Clearly the morphology of the interface is demonstrated by the complementary images.

**Results**

CuInSe\textsubscript{2} films were epitaxially grown on GaAs(111). The CuInSe\textsubscript{2}(112) surface is characterized in the LEED pattern by a 4x2 chalcopyrite related superstructure. After Se decaping the films showed in the PEEM protrusions in the µm range (Fig.2) for the image taken at the work function cut off. Fig. 5 shows the secondary on set images of the annealed sample for excitation with $\hbar\omega=4.9\text{eV}$ and $\hbar\omega=400\text{eV}$. As indicated by the arrows and circles the exciting light is incident from opposite directions for the two used photon energies. The dark streaks can thus be explained by shadows of protrusions growing out of the sample. In addition intensity variations show an inhomogenity of the sample surface with respect to the workfunction. Focusing for lower photon energies on small protrusions is difficult due to the high voltage between sample and objective lens and the lightning rod effect. This explains the less sharp image of the shadows for the 4.9eV excited image in Fig 2.
Fig 2. PEEM images of the CuInSe₂–ZnSe-ZnO interface as shown for the workfunction contrast for photon energies of 4.9eV (left) and 400eV (right). The arrows give the incidence direction of the photons. Circles show areas where the shadows clearly follow the direction of the incident light. Field of view is 50µm.

Energy filtered images (Fig.3) taken on the Cu3d valence band emission, the In 4d level and the Se 3d emission demonstrate that the protrusions show a deficiency in In and enrichment in Cu while the Se is evenly distributed. By closer inspection of the feature e.g. marked by the white circle the bright area left of the shadow in the Cu3d image is dark in the In 4d emission pattern whereas the Se 3d shadow has the same appearance as in the image taken at the kinetic energy of Cu 3d valence band structure 6/. As Cu₂-₅Se is known to segregate at the surface of Cu rich prepared CuInSe₂ films 8/ here we have the direct observation of the segregation and can show that they form clusters at the surface.

Fig. 3 XPEEM images of a pristine Cu-rich CuInSe₂ (112) surface after Se decaping in the microscope. From left to right the images are taken on the Cu 3d valence band emission, the In 4d emission and the Se 3d emission. The circle highlights an area where the shadow and the right part of the protrusion show clearly differences between the Cu and In image whereas the Cu and Se image exhibit a similar shape. FOW =50µm.
Fig 4 shows the LEED pattern for a growth sequence of MOMBE ZnO on CuInSe$_2$. After the first deposition steps the pattern changes to a 1x1 structure which is attributed to the growth of ZnSe (see Fig 4). Further exposure to DEZ + H$_2$O will start the ZnO growth as indicated by the additional LEED pattern of ZnO. Remarkable is the oriented, single crystalline ZnO growth despite the large lattice mismatch in registry to the substrate, showing the high quality of the interface.

![LEED patterns](image)

Fig 4 LEED pattern in the course of DEZ-H$_2$O exposure.

In Fig 5 the Photoelectron spectra in the course of ZnO deposition are displayed. As for the first deposition steps no O1s signal is detected, it is concluded from the Auger-parameter (not shown) and LEED pattern, that a thin epitaxial ZnSe film is growing before the ZnO growth takes place. In addition the band bending in the substrate is clearly observe as a shift in the substrate core level emissions.

![Photoelectron spectra](image)

Fig 5 XPS core level spectra in the course of DEZ-H$_2$O exposure. MOMBE ZnO growth temperature is 450°C

The evaluation of the photoemission intensities for the ZnO deposition indicates a layer by layer growth mode.

The drastic reduction in the Cu intensity can be explained by the creation of an ordered vacancy compound (OVC) in the CuInSe$_2$ contact phase /7/. At higher ZnO coverages an In signal is reappearing in the spectra of the thick ZnO-overlayer indicating a diffusion of In through the interface. The binding energy of the In 3d emission is indicating an InO$_x$ layer. To study the interface in more detail the sample was transferred to the XPEEM.
and images were taken at the secondary on set and the core level energies of Zn3d, In 3d and 01s.

In Fig 6 images are taken on the relevant core levels. It is clearly seen that areas were In is found the Zn intensity is lower and vice versa, whereas the 01s intensity is not varying significantly.

![XPEEM Images](image)

**Fig.6** Synchrotron excited XPEEM images taken at the given photon energies and kinetic energies of the imaging analyser. Field of view is 50µm.

Whereas the spectroscopic data in Fig. 5 give no information on the spatial distribution, the XPEEM images clearly show an In diffusion preferentially at the sites where the protrusions are located. The height of the protrusions can be estimated to be up to 1µm in height as given from by the length of the shadow and the angle of incidence of the light. Even if the sample displays a perfect LEED pattern, indicating epitaxial growth, it must be concluded that an InOx is contributing to the electronic properties of the interface. As a group III element In on a Zn site will enhance the n-type doping of the ZnO film. On the other hand the distribution of In and Zn in the XPEEM images suggests an In concentration which is beyond a doping effect.

/2/ E. Brüche, Z. Phys. 86, 448, (1933)
/7/ Pohl Johan; Klein Andreas; Albe Karsten;Phys. Rev. B 84, 121201 (2011)