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$CuGaSe_2$ - $CuGa_3Se_5$ phase transition in CCSVT-grown thin films

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Abstract

The system $CuGaSe_2$ - $CuGa_3Se_5$ in thin films has been investigated. Layer synthesis was carried out by chemical close-spaced vapour transport (CCSVT) using Cu precursors on Mo/soda-lime glass substrates. The extension of deposition times in a two-step process led to final film compositions with [Ga]/[Cu] ratios ranging from 1 to 3, allowing the study of the phase transition mentioned above. Films showing chalcopyrite (1:1:2), OVC (1:3:5) and two-phase were grown. X-ray emission spectroscopy and x-ray diffraction (XRD) techniques have been combined for a compositional and structural study of this material system probing both bulk and near surface properties of the films. This analysis was also extended to the rear-surface investigation of selected two-phase thin films and complemented with surface sensitive photoelectron spectroscopy (PES). From these results a growth model is presented for $CuGa_3Se_5$ formation in gallium-rich, CCSVT-grown $CuGa_xSe_y$-films.

Introduction

Copper-containing chalcopyrites are interesting materials for photovoltaic applications. They can be roughly clasified in low- (1.0 eV – 1.3 eV; $CuInSe_2$, $Cu(In,Ga)Se_2$ with low gallium content) and high-gap (1.3 eV – 2.4 eV; $CuGaSe_2$, $CuInS_2$, $CuGaS_2$) materials. The latter group offers promising candidates for the realization of high-voltage solar cell devices and of top cells in tandem configuration. Whereas the interface between low-gap absorbers and buffer layers does not seem to be a critical issue for device performance, those based on wide-gap absorbers, suffer from electronic losses related to interfacial issues. It is generally accepted that the presence of secondary phases in the absorber surface stemming from copper depletion (Ordered Vacancy Compound (OVC) defect chalcopyrite) play a major role in the interface electronics with a positive impact in low-gap-based devices originating from band-gap widening and type inversion in the near surface region of the absorber [1]. For the particular case of $CuGaSe_2$, evidence of band gap widening has been reported [2] together with deviation from stoichiometry pointing to formation of OVC-related phases. However, the positive impact of OVC surface phases seems to be minor in wide-gap absorbers and there is additionally a general lack of knowledge of fundamental properties regarding growth, structural and electronic properties at the interface of $CuGa_xSe_y$ device-quality material. As long as these OVC-like phases mediate the interface formation it is of highest importance to study this material system. In this investigation we focus our attention on the growth, compositional and structural properties of chemical close-spaced vapour transport (CCSVT)-grown $CuGa_xSe_y$ thin films as a function of gallium and selenium enrichment, as this is considered to be the key for optimizing the formation of the absorber/buffer interface. Bulk [x-ray fluorescence (XRF) and x-ray diffraction (XRD) in θ-2θ mode], near surface [soft x-ray emission spectroscopy (SXES) and grazing incident (GI)-XRD] and surface sensitive [photoelectron spectroscopy (PES)] methods allow the identification of compositional

variations at these three different levels of information depth, which are correlated with structural modifications.

Experimental

$CuGa_xSe_y$ thin films were grown by CCSVT [3] in a compositional range of $1 < x < 3$. This was performed by a variation of deposition times. For analysis of the rear-side a glass substrate was glued with silver-epoxy on the top side of the layer of selected structures ($CuGa_xSe_y$/Mo/soda-lime glass). Afterwards the layer was lifted-off [4] under inert N_2-atmosphere.

X-ray fluorescence (XRF) for integral compositional studies was performed in a Phillips MagiXPro PW2440 system using 18keV Rhodium K-radiation as excitation source and the SuperQ software for subsequent calculations. For this purpose Ga and Cu K-lines have been used. Theoretical calculation of absolute attenuation lengths for these emission energies gives values of approx. 10µm [5]. Those are well above the overall layer thickness for the samples, typically 1-3µm, and hence provide integrated compositional information.

Soft x-ray emission spectroscopy (SXES) analysis and photoelectron spectroscopy (PES) were carried out in the spectroscopic system "CISSY" (for a more detailed description see [6]) at the U41 PGM high-flux beam line at BESSY II. In this investigation SXES was performed with an excitation energy of $E_{phot.}$=1200eV for recording Cu and Ga L_2 emission lines using a SXES 300 Scienta Gammadata spectrometer. Referenced values for Ga L_2 at 1097.9eV and Cu L_2 at 929.7eV [7] were used to set the energy scale. The attenuation length for these emission energies is approx. 300nm [5]. This means that SXES provides more surface related compositional information compared to XRF.

A CLAM4 electron spectrometer (Thermo VG Scientific) was used for PES experiments. The zero point of the energy scale for $h\nu=174eV$ was set so that the Au $4f_{7/2}$ reference line appeared at a binding energy of 84.00eV [8].

Structural film characterization was performed by means of X-ray diffraction using a Bruker D8 Advance X-ray diffractometer with monochromatized Cu-K_a radiation including a Goebel mirror in the primary beam for parallel beam optics. The system was operated at 40kV and 40mA in ? - 2? and Grazing Incident (GI) mode, the latter with an incident angle of 0.8°.

Results

The films selected for SXES investigation show integral atomic [Ga]/[Cu] ratios as measured by XRF of 1.0, 1.2, 1.7 and 2.6 respectively. Cu L_2 and Ga L_2 emission lines detected from the front surfaces of the layers are shown in Fig.1 where the Cu L_2 peak was used to normalise all spectra. The Ga L_2 emission intensity increases with higher integral [Ga]/[Cu] ratio as expected.

In order to compare vertical compositional gradients in the $CuGa_xSe_y$ (with x=1.7 and 2.6) samples, SXES spectra were additionally recorded from the rear surface after lift-off of these $CuGa_xSe_y$ films, as shown in Fig.2 normalised to Cu L_2 intensities. For further comparisons the nearly stoichiometric sample with an integral x=1.0 served as a reference, assuming a homogeneous distribution of gallium and copper, at least throughout the film thickness probed by SXES. The normalised Ga L_2 reference spectra multiplied by the XRF-determined [Ga]/[Cu] ratios is shown in Fig.2 (squares) together with the detected spectra both from front (dotted) and rear surface (solid). It can be observed that the Ga L_2 intensity measured from front surface is higher than that recorded for the rear surface. This fact indicates that the front surface region is gallium richer than the backside of the thin films. When comparing measured with calculated spectra for the x=2.6 film it turns out that the integral composition lies at mid-values between the contributions determined from front and rear sides pointing

either to a double layered structure or a vertical gallium gradient through the layer. For the

x=1.7 film the rear-side Ga L_2 emission line shows nearly the same intensity as the calculated

curve. The measured front side peak intensity clearly exceeds that from the calculation. This

strengthens the assumption of a bi-layer structure formation which is further supported by

XRD measurements, as discussed in the following. Detailed calculations of absolute

[Ga]/[Cu] ratios revealed from SXES spectra, which should include the effect of both surface

roughness and compositional gradient related issues, are in progress.

XRD measurements in θ - 2θ and grazing incident (GI) mode were performed obtaining

structural information from the bulk and near surface regions. The GI angle was set to 0.8° in

order to achieve comparable information depths as those probed by SXES, as discussed above

[5]. Only two phases, attributed to $CuGaSe_2$ chalcopyrite [9] and $CuGa_3Se_5$ Ordered Vacancy

Compound (OVC) [10] have been observed in all θ - 2θ measurements (see Fig.3).

Evidence of additional phases like $Cu_{2-x}Se$ or Ga_2Se_3 has not been found in any of the

investigated films. For $CuGa_xSe_y$ film compositions close to the 1:1:2 stoichiometry with

x=1.0-1.2 the XRD spectra only show peaks which can be attributed to the 1:1:2 phase with

chalcopyrite structure. For gallium-richer layers (x=1.7-2.6) additional diffraction peaks

attributed to the 1:3:5 OVC phase also occur. Their contribution increases with higher overall

gallium content. No 1:1:2 related peaks are detected for x=3 (see Fig.3). The shift of

identically indexed reflexes to higher diffraction angles of 1:3:5 peaks than the corresponding

1:1:2 peaks is associated with a reduction of the lattice parameters ($CuGa_3Se_5$: a_0=0.550nm

and c_0=1.095nm [10] $CuGaSe_2$: a_0=0.561nm and c_0=1.1032nm [9]).

Fig.4 shows the highest intensity peak of both phases, the (112), comparing θ - 2θ and GI-

XRD measurements. No features from 1:3:5 phase have been observed for x=1.0-1.2 neither

in the bulk nor in the near surface region. In turn, for x=3.0 no 1:1:2 phase related peaks have

been observed within the resolution of this method. The two films with x=1.7 and 2.6, where

the 1:3:5 and 1:1:2 phases coexist, are of special interest for the establishment of the growth

model. For this purpose the (112) peaks of both phases were fitted (see Fig.4) with a Pearson VII function including Cu-$K_{\alpha 1}$ and -$K_{\alpha 2}$ contributions. The intensity ratios of (112) 1:3:5/(112) 1:1:2 varies between ? - 2? and GI modes with a higher 1:3:5 contribution for more surface sensitive GI measurements.

The CuGa$_x$Se$_y$ thin film with x=1.2 is moderately gallium rich, but even surface sensitive GI-XRD cannot prove the existence of the 1:3:5 structure in the near surface region of the sample. Additional PES measurements were performed, recording Cu 3p, Se 3d and Ga 3d lines (not shown). The surface composition was calculated from integrated line intensities (after fitting with a Voigt function) and corresponding cross sections [11]. From these results a surface composition of CuGa$_{3.1}$Se$_{5.6}$ at least for the first 2-3 monolayers surveyed by this technique [12] is determined. This indicates that a copper depleted surface region of the type 1:3:5 is formed in moderately gallium rich CCSVT-grown samples, in accordance to previous results [13].

Discussion

A growth model of gallium rich phases in CCSVT-grown CuGa$_x$Se$_y$ thin films can be proposed based on these results. The use of bulk (XRF and XRD in θ-2θ mode), near surface (SXES and GI-XRD) and surface sensitive (PES) methods allows the identification of compositional variations at these three different levels, which are correlated with structural modifications. A few monolayer thick copper depleted surface region is formed on bulk single phase 1:1:2 films. This surface layer promotes the formation of a 1:3:5 near-surface region with further gallium and selenium enrichment for x>1.7. This transition is directional from the front to the bottom of the films. No evidence of 1:1:2 remnants was found for an integral bulk composition of x=3.0. Hints of surface copper depletion in 1:3:5 phase suggests this to be an intrinsic surface relaxation mechanism, which may in turn lead to a gallium- and selenium-

richer OVC phase formation with further gallium and selenium enrichment, particularly 1:5:8, as has been already reported e.g. in [14] for PVD grown samples.

Conclusions

The transition between the 1:1:2 phase and the 1:3:5 phase in CCSVT-grown $CuGa_xSe_y$ thin films has been monitored. A bi-layer structure consisting of a near surface 1:3:5 phase covering a 1:1:2 bulk phase has been found for $1.7<x<2.6$. The transition region between these two phases moves towards the rear side with increasing gallium content, until the complete layer shows OVC structure for $x=3.0$. Additionally, copper depletion has been found at the surface of the samples.

Acknowledgement

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figure captions

Fig.1: Cu L_2 (left) and Ga L_2 emission lines (right) observed by SXES (hν=1200eV) from front-side measurements of CCSVT grown $CuGa_xSe_y$ thin films with different integral XRF-determined [Ga]/[Cu] ratios x. All spectra were normalised to the Cu L_2 intensity. An increase in the intensity of the Ga L_2 emission is clearly correlated with the integral gallium content of the layer.

Fig.2: Comparison of SXES Cu L_2 (left) and Ga L_2 (right) emission lines for two gallium rich $CuGa_xSe_y$ thin films with integral [Ga]/[Cu] ratios of x=1.7 (upper panels) and 2.6 (lower panels) respectively, as observed from front (dotted) and lifted-off rear sides (solid). All spectra were normalised to the Cu L_2 line intensity. Calculated Ga L_2 lines(squares) were obtained by multiplying normalised reference spectra (x=1.0) by XRF-determined [Ga]/[Cu] ratios.

Fig.3: XRD ? -2 ? scans of $CuGa_xSe_y$ thin films with XRF-determined integral compositions in the range of 1<x<3. Single phase 1:1:2 (lower panel) [8] (vertical lines) and single phase 1:3:5 [9] (filled circles) (upper panel) for x=1.0 and x=3.0 respectively are observed. Both phases are identified for intermediate compositions.

Fig.4: Comparison of (112) reflexes of thin $CuGa_xSe_y$ films, in the integral XRF-determined compositional range of 1<x<3, measured in ? -2 ? - (lower panels) and GI-mode (0.8°) (upper panels). For bi-layer samples two (112) peaks can be resolved, the (112) of the 1:3:5 phase at higher (2?~28.1°) and the (112) of the 1:1:2 phase at lower (2 ? ~27.7°) diffraction angles. These two films (x=1.7/2.6) show a higher contribution of the 1:3:5 phase in surface sensitive mode (upper panels).
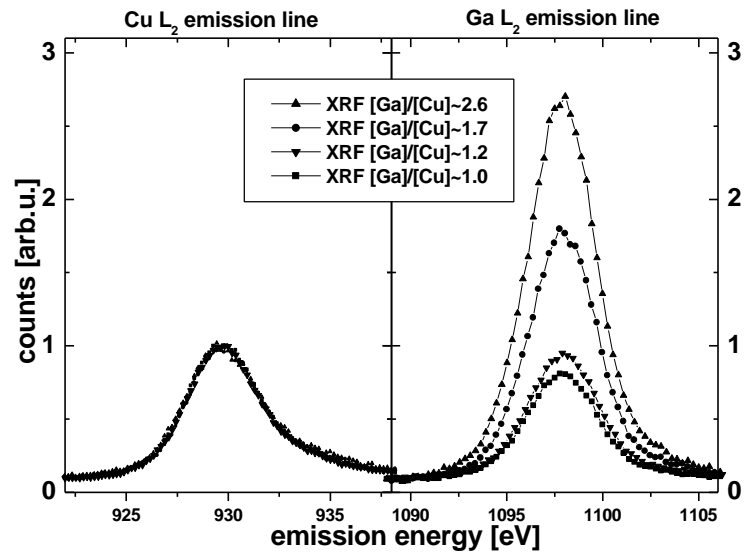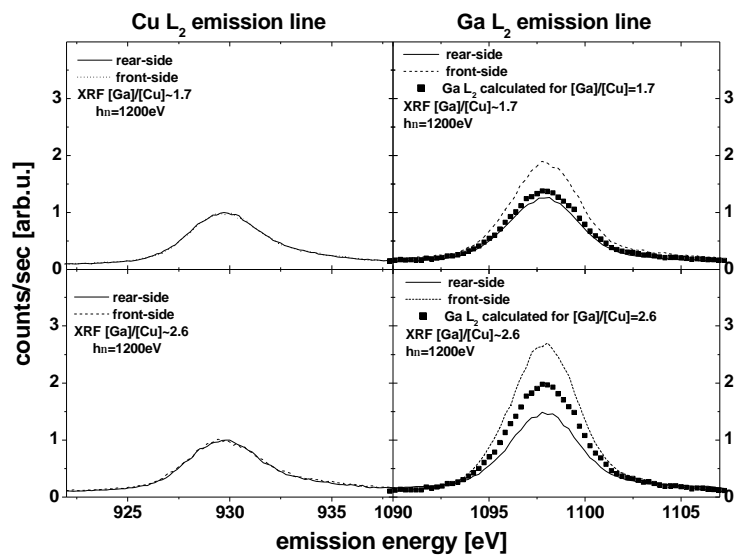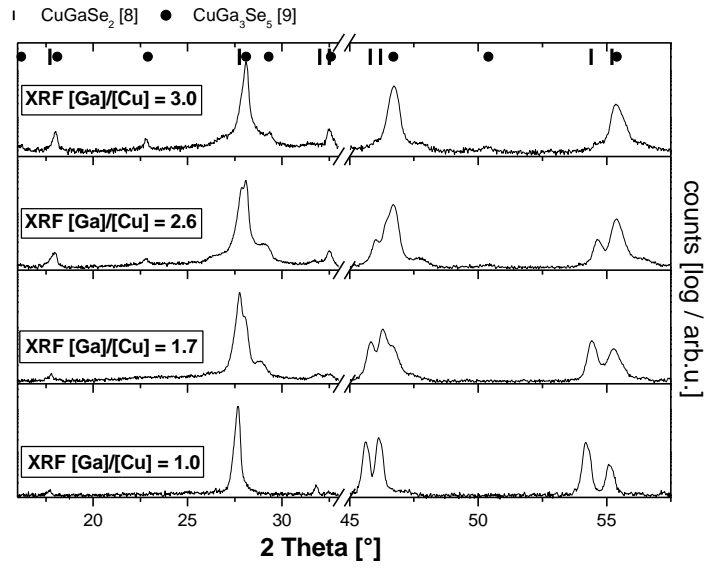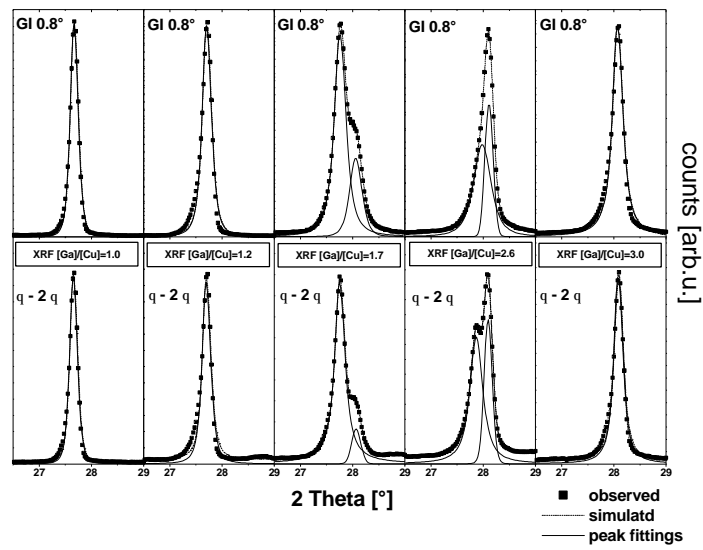
Figure 1

Figure 2

Figure 3

Figure 4