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Raman spectroscopy for quality control and process optimization of chalcopyrite thin films and devices

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Abstract

We will demonstrate in this paper that Raman scattering of visible light is a versatile tool both for research and industrial process monitoring of thin chalcopyrite films for solar cells. Thin films of Cu(In, Ga)(S,Se)$_2$ (CIGSSe) are produced by rapid thermal processing of stacked elemental Cu–In–Ga–Se layers. The Raman investigations are accompanied by grazing incidence X-ray diffraction (GI–XRD) and X-ray florescence (XRF) measurements. GI–XRD measurements confirm that the films show a two-fold elemental gradient: a sulfur gradient from the top and a Ga gradient from the CIGSSe/Mo interface. By Rietveld refinement of the GI–XRD spectra of the surface–near (~ 100nm) ratio of sulfur to selenium can be obtained which corresponds well to the intensity ratio of the two Raman A1 modes of $CuInS_2$ and $CuInSe_2$. The asymmetric line shape of both XRD diffractograms and Raman spectra is attributed to the sulfur gradient. In addition we show that the intensity ratio of the satellite Raman B and E modes shows a correlation with the Cu to In+Ga ratio obtained by XRF.
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1. Introduction

Thin films of Cu(In,Ga)(S,Se)$_2$ show excellent properties as absorber layers for ZnO/CdS/CIGSSe hetero-junction solar cells and modules. At Shell Solar Munich a second generation process for large area, in-line industrial processing has been developed: on a soda lime glass substrate coated with a SiN-barrier layer and a Mo-back electrode a Na-precursor and a multilayer stack of Cu (Ga) and In are deposited by magnetron sputtering, followed by elemental Se by thermal evaporation. The complete stack is processed to CIGSSe by rapid thermal processing (RTP) in a sulfur containing ambient [1]. Both for R&D work and for the commercial production of thin film devices a tight process control is mandatory. We recently demonstrated that Raman spectroscopy can be applied to monitor the S/Se ratio in CIGSSe absorber layers [2,3]. In this work we present a more detailed analysis of Raman spectra for CIGSSe films with different sulfur content by comparing the results from Raman spectroscopy with GI–XRD measurements. In addition we present an interesting correlation between two Raman satellite modes and the cation stoichiometry ratio Cu/(In+Ga).

2. Experimental

CIGSSE films with different sulfur content were produced by varying temperature, reactive gas flow and time of the RTP process. The Raman measurements have been performed using a Jobin Yvon LabRam micro-Raman spectrometer, with identical measurement parameters as described in [3]. After subtracting a linear baseline from the measured spectra, we calculated the ratio of the area integrals from 235 cm^{-1} to 370 cm^{-1} for the S group of lines (denoted Int(S)) and from 145 cm^{-1} to 235 cm^{-1} for the selenium lines (Int(Se)). These integration ranges comprise the A1 mode as well as the satellite peaks that are attributed to the B and E modes [4]. For the measurement of the integral composition a Bruker SHS 3400 X-ray florescence spectrometer is used. The atomic concentrations are determined by a thin film model (Bruker software) that is calibrated to ICP (inductively coupled plasma

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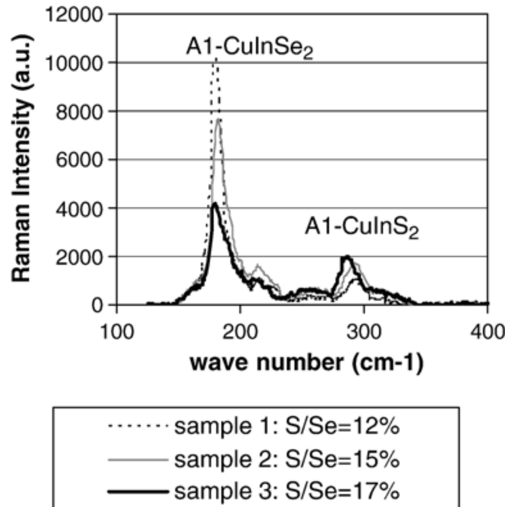

Fig. 1. Raman spectra of three CIGSSe thin films with different sulfur content (as determined from XRF). Inset: detail around $A1^{Se-Se}$ normalized to maximum for all three spectra.

analysis). For a comparison in view of phase composition and structure the samples have been analyzed by X-ray diffraction with a Philips X'Pert Pro-MPD powder diffractometer (tube settings U=45 kV, I=40 mA). In order to obtain surface sensitivity, the diffraction patterns were recorded in gracing incidence geometry. In this setup, the X-ray tube is equipped with a multilayer mirror optics to obtain a parallel and monochromatic X-ray beam (Cu–Kα radiation). The detection system consists of a parallel plate collimator followed by a graphite monochromator and a proportional detector. A variation of the incidence angle ω enables depth profiling of the absorber layer. The depth profiles as shown in 3.2 have been recorded with ω=0°, 0.25°, 0.50° ... 2.00°. In order to apply GI–XRD to the rear side of the sample, CIGSSe films were mechanically removed from the Mo back electrode. The GI–XRD measurements from top and rear side are compared to a Bragg-Brentano measurement of the same sample, which delivers diffraction contribution of the entire thickness of the absorber layer. In order to determine the S/(Se+S) ratio in CIGSSe on the top surface as described in 3.3, the incidence angle of these GI–XRD measurements was chosen to be ω= 0.13. This incidence angle corresponds to a penetration depth of Cu-Kα radiation of about 100 nm in CIGSSe, which enables a comparison of the resulting S/(Se+S) with the value determined by Raman spectroscopy. Diffraction patterns were recorded in the 2θ-range between 15° and 55° with a step size Δ(2θ)=0.03°. The diffraction patterns were refined with the Rietveld method [5]. The observed asymmetry on the high-angle side of the Bragg reflections of the chalcopyrite originates from an inhomogeneous sulfur distribution in the $Cu(In,Ga)(S,Se)_2$ mixed crystal, see section 3.2. For this reason, a secondary phase of $Cu(In,Ga)S_2$ together with the main phase $Cu(In,Ga)(S,Se)_2$ was included in the refinement process. A partial substitution of selenium with sulfur on the anion site of the chalcopyrite main phase has been allowed in the refinement procedure. These values deliver the sulfur content S/(Se+S) in the surface-near region (about 100nm) of the main phase $Cu(In,Ga)(S,Se)_2$.

3. Results and discussion

3.1. Raman spectra of cigsse films with different sulfur content

Fig. 1 shows Raman spectra of three samples with different total sulfur content (XRF). As shown previously [2–4] the dominating peak around 180 cm^{-1} is attributed to the A1 mode of anion vibrations in $CuInSe_2$. The dominating peak in the second group at 290 cm^{-1} is attributed to the A1 mode in $CuInS_2$. The coexistence of both groups of bands, i.e. a bimodal behavior, has been observed also for homogeneously $CuIn(S,Se)_2$ mixed crystals [6]. Both groups would also be expected if sulfur rich and sulfur poor phases lie within the detection volume. A higher total S/Se ratio (XRF) leads to an increase of the ratio Int(S)/Int (Se) and of the line width of the dominating peak around 180cm^{-1}. As shown previously, $Cu(In,Ga)(S,Se)_2$ films prepared by rapid thermal annealing of stacked elemental layers indeed show a sulfur gradient in the surface region [2,7]. In the next section this surface region will be analyzed by GI–XRD.

3.2. Analysis of front and back side by Grazing Incidence XRD

The depth profile analysis of a typical CIGSSe sample is shown in Fig. 2. The Bragg–Brentano measurement, indicated with (a), shows the 112- and 103 reflections of quasi Ga-free $CuInSe_2$. A third peak in between can be attributed to the 112 reflection of a Ga-rich phase, described as $CuGaSe_2$ in the figure. The group (b) of diffraction patterns consists of GI–XRD measurements of the rear side (Mo/CIGSSe interface) with different incidence angles ω between 0° (bottom of group (b)) and 2.0° (top of group (b)). The GI–XRD measurements of the top surface are shown in group (c). A comparison of group (b) and (c) diffractograms demonstrates that the Ga-rich phase is enriched on the rear side: the 112-$CuGaSe_2$ reflection can not be observed in GI–XRD measurements of the top surface. The intensity ratio of 112-$CuGaSe_2$ to 112-$CuInSe_2$ decreases with increasing penetration depth within group (b), which shows a

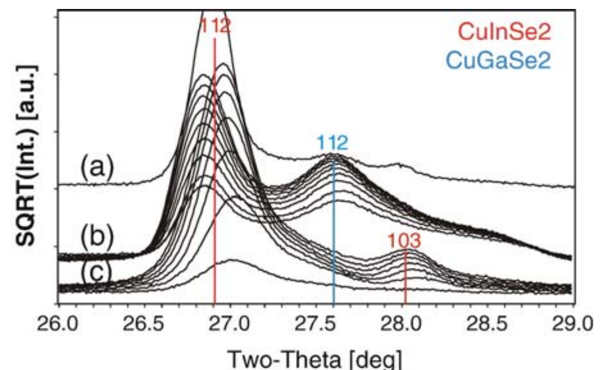

Fig. 2. Diffraction patterns of a typical CIGSSe sample: (a) Bragg-Brentano measurement, (b) GI–XRD from backside (Mo/CIGSSe interface) and (c) GI–XRD from top surface.

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