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Characterization of kesterite thin films fabricated by rapid thermal processing of stacked elemental layers using spatially resolved cathodoluminescence

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ABSTRACT

We report on the microstructure analysis of kesterite ($Cu_2ZnSnSe_4$) layers from rapid thermal processing of sequential elemental layers by spatially resolved cathodoluminescence in a scanning electron microscope. Energy dispersive X-ray fluorescence, X-ray diffraction and Raman spectroscopy were carried out for the validation of the findings. Special emphasis is put on the discussion of the occurrence of the secondary phases Cu_2SnSe_3, Cu_2Se, ZnSe and SnSe.

1. Introduction

In the kesterite ($Cu_2ZnSn(S_{1-x}Se_x)_4$ or in brief CZTS(e)) thin film solar cell material, the origin of major efficiency limiting factors is widely investigated since recent years. As a successor material of the well-established chalcopyrite (record cells yielding above 20% [1] and modules above 15% [2] efficiency) the physical origin of the detrimental performance in the case of kesterites (best cell efficiencies lie in the 12% to 13% range [3]) is still under intense study. Like in all microcrystalline solar cells, the microstructure and morphology of the absorber material, in particular grain boundaries and in the case of compound semiconductors, secondary phases are of great importance. In addition, point defects strongly determine the overall device performance. In this work the "bulk" electronic properties of the solar cell absorber are addressed using cathodoluminescence (CL). In general, luminescence studies allow the non-destructive investigation of electron hole pair transitions via direct band gap, as well as below band gap defect or material disorder related phenomena. Hence, the presence of the desired CZTSe phase or the detection of secondary phases, as well as point defects should be possible by luminescence. Performing CL studies in a scanning electron microscope (SEM) has the advantage, that simultaneous studies of the layer microstructure are possible so that correlations can be conducted. In CZTS and CZTSe, so far, the correlation of CL and photoluminescence (PL) and defects seems to be rather difficult or even impossible. As pointed out in two review articles by Siebentritt et al. [4,5], disorder on an atomic scale, as well as high concentration of native point defects make it rather difficult to determine their exact energetic level or to identify secondary phases within the broad luminescence spectra. Therefore, there is only a limited knowledge on the luminescence fingerprint of various CTZS(e) properties available in literature, compared to other traditional or even novel semiconductor materials. (Temperature dependent) Optical absorption [5] with low spatial resolution in the mm range was often applied to study the optical bandgap of CZTS and semiconducting secondary phases. Altogether, there is only limited literature available that focus on optical spectroscopy of CZTS(e); often luminescence data on certain defects are published in the frame of extended electro-optical studies where optical spectroscopy played a side role. Nevertheless, even with limited reference data, the study of CZTSe using CL with a spatial resolution on the μm-scale is believed to be valuable for better understanding of the physical layer properties.

In this work we report on the microstructure analysis of kesterite layers from rapid thermal processing of sequential elemental layers (RTP-SEL) by spatially resolved CL in a SEM carried out at room temperature. In addition, energy dispersive X-ray fluorescence (EDX), X-ray diffraction (XRD) and Raman spectroscopy were carried out for the validation of the findings. In the discussion we will put special emphasis on CZTSe and the secondary phases Cu_2SnSe_3, Cu_2Se, ZnSe and SnSe. Intrinsic point defects are not discussed in this work.

2. Experiments

2.1. Sample preparation

Kesterite thin film samples were prepared on float glass by DC magnetron sputtering of the Mo back side electrode (thickness = 400 nm)

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and the absorber layer components Cu (thickness = 175 nm), Zn (thickness = 155 nm), Sn (thickness = 230 nm) under Cu-poor ([Cu]/([Zn] + [Sn]) = 0.8) and Zn-rich ([Zn]/[Sn] = 1.2) conditions. Layer thickness was controlled by the calibration of the sputter setup prior deposition with test samples and in addition verified by post-deposition weighing of the samples. The target purity was 4 N. To study the secondary phase formation, the layer sequence of Cu, Zn and Sn was varied in three ways (Table 1). The chalcogen Se (thickness = 2 μm) was thermally evaporated in excess on top of the metallic layers. Rapid thermal annealing was carried out for all samples at ca. 550 °C for 5 min in a quartz tube furnace under nitrogen ambient. A quasi-closed graphite box with a graphite foil on top of the sample served as an annealing container. Heating up was performed with the graphite box inside the oven using a temperature ramp of ca. 15 °C/min to 30 °C/min which coincides with our typical differential scanning calorimetry experiments (not addressed within this work). Cooling down was carried out by pulling the graphite box out of the hot zone; the initial temperature ramp was up to 30 °C/min. The total gas pressure inside the graphite box is unknown. Subsequent to annealing, the samples were surface passivized using a CdS nanoparticle deposition [6]. The final sample thicknesses lie in the range of 2.5 μm to 3 μm as confirmed by cross sectional SEM (without Fig.).

2.2. Characterization methods

Before examining the samples in a JEOL JSM 6400 scanning electron microscope, carbon coating using a JEOL JEC-530 coater was carried out to reduce charging of the investigated samples. SEM images were acquired in the secondary electron (SE) and back scattered electron (BSE) modes at a 20 kV electron acceleration voltage. Spectrally resolved CL was measured using a Jobin Yvon HORIBA Triax 552 spectrometer equipped with a 150 grid and silicon CCD detector for visible and ultraviolet light. For the near infrared light a 950 grid and InGaAs line detector was used. CL measurements were carried out at room temperature. However, the experimental setup is equipped with a flow-through stage for cooling down the sample chuck to 10 K or 70 K using liquid helium or liquid nitrogen. The CL system contains an automated luminescence peak analysis tool as well as a 2D topographic mapping routine. In this study CL spectra were acquired while continuously scanning the electron beam at a SEM magnification of 140 or 150 over a ca. 0.6 mm^2 square window. At the acceleration voltage of 20 keV the maximum electron beam penetration depth in CTZSe like materials lies in the range of 2.5 μm to 3 μm which coincides with the sample thickness. The maximum electron beam current was chosen to be 0.4 μA. At greater currents (e.g. 0.9 μA or 2.1 μA, see Fig. 1) or smaller scanning areas, a too high current density and, hence, energy deposition in the measurement field leads to sample degradation. This is most likely attributed to the partial evaporation of the CdS passivation capping layer. A similar behavior has also been observed in a former study [7], carrying out micro-PL of $CuIn_xGa_{1-x}Se_2$. Unintentional carbon deposition from residual gases inside the SEM which would also cause a similar image change cannot be excluded but reference measurements on bulk GaAs material without surface degradation effect underline the above-mentioned degradation behavior. In a previous work on CL on organic semiconductor materials [8] we have shown that the application of a short time pulsed measurement mode may prevent the layer degradation within the CL signal acquisition time.

EDX measurements were carried out using a Noran Instruments D-2786 and Fondis Electronic DXP-X10P Digital X-Ray Processor setup. For the quantitative analysis of the EDX spectra the software package IDFix was used. In order to excite the high-energy K lines of the elements Cu and Zn the electron acceleration voltage was set to the maximum value of 20 kV.

Raman spectra were measured using a confocal micro-Raman setup HORIBA (LabRam HR Evolution — HORIBA) and the software package LabSpec 6. As laser sources a green Nd-YAG (532.1 nm) device and a red HeNe (632.8 nm) device of ca. 1 mW power were used. In the case of microscope magnification of 50 the nominal laser spot diameter was 1 μm. The measurement time was 15 s for each sample location; no indication of thermally induced effects on the Raman spectra was observed. This coincides well with other reports like in Djemour et al. [9] who even used triple of the laser excitation density.

XRD data were acquired using a Bragg–Brentano setup (X'pert Pro MPD, Phillips) and the Cu kα line of a 40 kV X-ray tube (tube current = 35 mA).

3. Results and discussion

Using the InGaAs detector, CL spectra in the optical transition range between 0.6 eV and 1.85 eV were acquired. In order to address secondary phases like ZnSe exhibiting a bandgap around 2.7 eV [10], the Si based detector was used with a spectral energy range between 1.1 eV and 4.0 eV. Fig. 2 shows two room temperature CL spectra of sample 1. In the measurement using the InGaAs detector (Fig. 2a) a CL onset is visible at 0.8 eV followed by a broad emission around 1.3 eV exhibiting a number of distinct transitions and a second lower emission band located around 1.8 eV. Using the Si detector (Fig. 2b) the emission at ca. 1.3 eV is reasonably reproduced. Additionally there is a very broad emission at ca, 2 eV which includes electronic transitions up to 2.5 eV. Due to lower Si detector quantum efficiency in the near infrared, luminescence spectrum below 1.2 eV is cut off. No electronic transitions are observed above 2.5 eV.

The observations in Fig. 2 are representative for all data of samples 1 to 3 listed in Table 1:

(i) No luminescence is observed above 2.5 eV. In sample 1 where X-ray diffraction and Raman spectroscopy give strong evidence for the existence of ZnSe as the secondary phase, CL does not show any fingerprint. The latter is attributed to the diffusion of excited electron hole pairs into the surrounding smaller bandgap material before radiative recombination. In addition, the "large area" measurement mode with an electron beam scanning area of 0.6 mm^2 may not be sensitive enough to detect a residual, low intensity luminescence of the ZnSe secondary phases. On the other hand, Djemour et al. [9] identified a broad emission line around 1.3 eV for ZnSe secondary phases using photoluminescence. Such emission may stem from defect related electronic transitions. However, in this study we do not find in CL a transition around 1.3 eV in sample 3 (see discussion below) that due to Raman spectroscopy should clearly exhibit the secondary phase ZnSe. The following discussion therefore focuses on electronic transitions related to the band gap of the material.

Table 1
Samples investigated.

Sample number	Layer sequence	Summary of identified material composition and phases by EDX, SEM and Raman (without Fig.)
1	Mo–Cu–Sn–Zn–Se	CZTSe (XRD, Raman) SnSe (XRD, EDX) ZnSe (XRD: as shoulder, Raman: broad peak, EDX) $MoSe_2$ (XRD, BSE and EDX at the cross-section)
2	Mo–Sn–Zn–Cu–Se	Se deficiency observed by EDX CZTSe (XRD, Raman) Thinner CZTSe layer than sample 1 and 3 SnSe (XRD, EDX) ZnSe (Raman: broad peak, EDX) No $MoSe_2$ (XRD, BSE and EDX on the cross section)
3	Mo–Cu–Zn–Sn–Se	CZTSe (XRD, Raman) Cu_2Se (XRD, EDX) ZnSe (XRD: shoulder, Raman: broad peak, EDX) $MoSe_2$ (XRD, BSE and EDX at cross-section) No SnSe (XRD, Raman)

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