Thin Solid Films 608 (2016) 62–70

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Influence of selenium amount on the structural and electronic properties of $Cu(In,Ga)Se_2$ thin films and solar cells formed by the stacked elemental layer process

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ARTICLE INFO

Article history:
Received 7 September 2015
Received in revised form 28 February 2016
Accepted 8 April 2016
Available online 14 April 2016

Keywords:
$Cu(In,Ga)Se_2$
Stacked elemental layer
Diffusion

ABSTRACT

In the following article the influence of selenium supply on the stacked elemental layer process during the final annealing step is investigated. We find that the Se supply strongly influences the phase formation in the $Cu(In,Ga)Se_2$ resulting in a modified Ga/In distribution. The effects of Se supply on the structural and electronic properties of the films are reported. The solar cell performance has been investigated in detail using current voltage and external quantum efficiency measurements. We find that the chalcopyrite crystal formation is strongly influenced by the Se supply during the growth process. Furthermore the interdiffusion of Ga and In is accelerated with increasing Se amount. This has direct consequences on band gap and series resistance, which leads to changes in the values of short-circuit current density, open-circuit voltage and fill factor. The open-circuit voltage increases with increasing band gap of the $Cu(In,Ga)Se_2$, whereas the short-circuit current density decreases with increasing band gap. The fill factor is affected by the formation of $MoSe_2$ at the back contact. The experimental findings are compared with the theoretical efficiency limits calculated from the Shockley–Queisser model, and also with numerical 1D SCAPS simulations.

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1. Introduction

$Cu(In,Ga)Se_2$ (CIGSe) thin films are promising candidates for solar cell applications due to their ability to reach high efficiencies of almost 22% [1]. Additionally the thin CIGSe layers ($\cong 1.5-2\mu m$) ensure low-cost commercial production. One prominent method for large scale production consists of a two step process, which includes the sputtering of metallic Cu–Ga–In precursors and the selenization in Se vapor [2]. In the following paper the absorbers are grown with the stacked elemental layer (SEL) process where the elemental layers are deposited layer by layer at first, which is followed by a rapid thermal annealing. The reaction path is driven from the top which means that Se interacts with the metallic precursors and forms binary selenides [3]. $CuInSe_2$ (CISe) formation takes place at the interface between indium and copper selenides, while the formation of $CuGaSe_2$ (CGSe) is kinetically inhibited at first [4] followed by a later Ga-selenide in-diffusion. High temperatures lead to interdiffusion between the CISe and CGSe regimes and result in a more homogeneous CIGSe layer [5] but also high thermal stress in the thin films. It is well known that CuSe phase acts as a flux agent on top of the CIGSe during the growth process, which leads to a desirable grain growth and a homogeneous Ga/In distribution [6,7,8]. In general big grains are favorable in terms of reduced charge carrier recombinations at grain boundaries. Nevertheless, this CIGSe structure can lead to the formation of shunt paths caused by the highly conductive CuSe phase. Therefore, alternative concepts to obtain flat Ga/In profiles are of interest, like a Se post-treatment approach [9]. Another approach is via the formation of a liquid Se-phase above the CIGSe thin film, which promotes the Ga/In interdiffusion [10]. In this work, we investigate the Se dependent CIGSe phase formation in detail by conducting experiments with varying Se supply. The main focus is on the Ga/In profiles and inparticular the Ga amount near-surface since these parameters are known to have a large impact on the optoelectronic properties like the band gap (E_g) and the solar cell device parameters. The experimental results are compared with numerical modeling results of the cells derived from SCAPS simulations, which are based on the actual concentration profile of the individual cells.

2. Experimental procedure

Commercially available float glass is used as substrate and Na source during chalcopyrite formation. Via magnetron sputtering 500 nm molybdenum (Mo) back contact is deposited above the glass. The Mo back contact consists of a seed and a highly conducting layer [11]. Furthermore, the metallic precursor stacking CuGa and In is sequentially deposited via DC sputtering ($p \approx 10^{-3}$ mbar) with CuGa alloy and

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http://dx.doi.org/10.1016/j.tsf.2016.04.015
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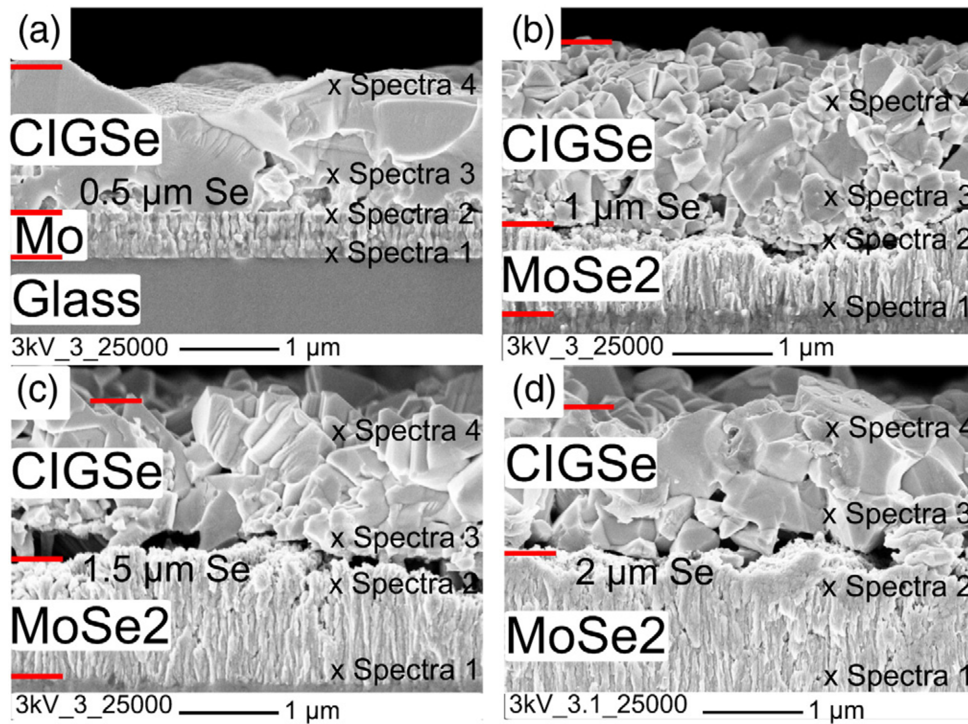

Fig. 1. SEM cross sections for different Se film thickness ranging from 0.5 μm (a) to 2 μm (d). The crosses at the thin film indicate the region of EDX analysis, which is written as Spectra 1, Spectra 2, Spectra 3 and Spectra 4.

elemental In target. In the next step elemental Se is evaporated (base pressure $p \approx 10^{-5}$ mbar) with a Knudsen cell on the metallic precursor layer with varying thicknesses from 0.5 μm to 2 μm. Afterwards, the whole sample stack is selenized in a N_2-Se vapor atmosphere (pressure regime between 700 and 800 mbar) in a closed graphite chamber. The glow discharge optical emission spectrometry (GDOES) depth profiling are performed by a GDA 550 from Spektruma Analytik with a CCD optical detection system under standard conditions [11]. Secondary electron microscopy (SEM) in cross sections are performed by a Zeiss 1530 system with energy dispersive X-ray (EDX) system (INCA Energy from Oxford Instruments). The accelaration voltage for imaging mode in secondary electron contrast is around 3 kV and for EDX spectra around 12 kV. The X-ray diffraction (XRD) investigations in Bragg Brentano geometry are realized by a Bruker D8Advance DaVinci-Cu (Cu–K_α-radiation with 40 kV and 50 mA). X-ray flourescence (XRF) measurements are performed with a XDV Fischerscope to analyze the integral material ratios present in the thin film. The spectral photoluminescence (PL) studies are done with a 830 nm excitation wavelength laser at room temperature (tilted geometry towards the film surface). For analyzing the electronic properties of the complete device, current voltage (I-V) and external quantum efficiency (EQE) measurements are performed.

Table 1
Evaluated Se/Mo, GGI, CGI and Se/metal ratios from EDX spectra of CIGSe/Mo films processed with different Se amounts. The different measurement points on the thin film are Spectra 1 (back contact/glass), Spectra 2 (absorber back side/back contact), Spectra 3 (absorber intermediate/absorber back side) and Spectra 4 (absorber top/absorber intermediate region).

0.5 μm	Se/Mo	GGI	CGI	Se/metal
Spectra 1	0.07	0.7	0.5	0.6
Spectra 2	0.61	0.86	0.69	0.88
Spectra 3	6.29	0.68	1.03	1.17
Spectra 4	29.33	0.21	1.58	1.42
1 μm	Se/Mo	GGI	CGI	Se/metal
Spectra 1	0.12	0.67	0.5	1
Spectra 2	3.34	0.78	0.78	7.31
Spectra 3	11.43	0.76	0.85	1.31
Spectra 4	35	0.25	1.75	1.59
1.5 μm	Se/Mo	GGI	CGI	Se/metal
Spectra 1	0.2	0.71	0.57	1.73
Spectra 2	3.61	0.78	0.67	8.67
Spectra 3	12.25	0.4	1.65	1.85
Spectra 4	31.67	0.55	0.95	1.28
2 μm	Se/Mo	GGI	CGI	Se/metal
Spectra 1	3.47	0.71	0.43	13.2
Spectra 2	3.62	0.75	0.75	8.79
Spectra 3	21.25	0.53	1	1.42
Spectra 4	36	0.39	1.3	1.36

3. Results and discussion

3.1. Structural investigation of the thin film

In Fig. 1 an overview of cross sections of the individual layers of the CIGSe structures obtained for different Se amount are shown. Furthermore a qualitative EDX analysis of the different layers are shown for different spectra in Table 1 (Spectra 1: back contact/glass, Spectra 2: absorber back side/back contact, Spectra 3: absorber intermediate/absorber back side, Spectra 4: absorber top/absorber intermediate region). In Fig. 1 (a,b) we can observe a strong

Table 2
GGI, CGI and Se/metal ratios of the CIGSe thin films determined via XRF for different Se film thicknesses, ranging from 0.5 μm towards 2 μm.

Se amount (μm)	GGI ratio	CGI ratio	Se/metal ratio
0.5	0.3 ± 0.01	0.98 ± 0.02	1.02 ± 0.027
1	0.26 ± 0.004	0.84 ± 0.01	1.77 ± 0.12
1.5	0.26 ± 0.006	0.84 ± 0.01	2.49 ± 0.18
2	0.24 ± 0.005	0.79 ± 0.008	2.6 ± 0.1

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