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Optical properties of reactively sputtered $\text{Cu}_2\text{ZnSnS}_4$ solar absorbers determined by spectroscopic ellipsometry and spectrophotometry

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ABSTRACT

We have determined for the first time the device-relevant optical constants of 500 nm and 800 nm-thick $\text{Cu}_2\text{ZnSnS}_4$ absorbers, grown on bare and Mo-coated soda-lime glass (SLG), using spectroscopic ellipsometry (SE). The composition, structure, phase purity and morphology were characterized by X-ray fluorescence, X-ray photoelectron spectroscopy depth profiling, X-ray diffraction, Raman spectroscopy, scanning-electron microscopy and atomic force microscopy. For the SE analysis, carefully determined sample characteristics were utilized to build a multilayer stack optical model, in order to derive the dielectric functions and refractive indices. The SE-derived absorption coefficients from CZTS/SLG samples were compared with those derived from complementary spectrophotometry measurements and found to be in good agreement. The bandgap determined from Tauc plots was $E_g = 1.57 \pm 0.02$ eV. The absorption coefficients just above the bandgap were found to be a few 10^4 cm^{-1} and to exceed 10^5 cm^{-1} at energies above ~ 2.5 eV, which is much higher than previously found. The sub-bandgap k -value was found to be $k \sim 0.05$ or less, suggesting that a moderate band tail is present. Separate device characterization performed on identical samples allowed us to assign device efficiencies of, respectively, 2.8% and 5.3% to the 500 nm and 800 nm-thick samples featured in this study.

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1. Introduction

The quaternary compound kesterite $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is a promising earth-abundant choice for thin film solar cell applications [1], owing to its direct bandgap of optimal size ~ 1.5 eV [2–5], its high absorption coefficient $> 10^4 \text{ cm}^{-1}$ in the visible region [2,3], as well as crystallographic and electronic structures similar to that of high-efficiency $\text{Cu}(\text{In,Ga})\text{Se}_2$ [6] based absorbers. Since the first 0.66%-efficient CZTS solar cell device made by Katagiri et al. in 1996, great progress was seen over the years [1,7]. The current efficiency records are $\sim 9.2\%$ for CZTS [8] and $\sim 12.6\%$ for its close relative CZTSSe [9]. However, more improvements are needed for CZTS to reach above $\sim 15\%$ in order to satisfy the requirements for practical applications. To understand the loss mechanisms and further improve the efficiency, electrical and optical device modeling [10,11] are needed. High-quality wavelength-dependent optical constants that accurately represent the device-relevant CZTS material are in demand as a crucial and a fundamental input if correct conclusions are to be drawn from such analyses. In general, optical constants, being fundamental material properties, are worth

being repeatedly determined for an important emerging material like CZTS.

So far, the existing literature ellipsometry data for the pure sulfide CZTS are limited [12–14] and have been deficient in one way or another: sample composition and description of surface preparation methods were sometimes lacking; the importance of careful material characterization was frequently overlooked; possible influences from secondary phases were often neglected; the analyzed absorbers were rarely grown in the same way or on the same substrates as those for devices; none have compared ellipsometry data with that from transmittance and reflectance measurements in the same study even though their transparent substrates permit such comparison. Furthermore, there is a general lack of comparable device performance values provided in the same study despite the generally observed spread in performance from different CZTS processing routes or even between nominally identical processes. To reach accurate conclusions from the complex optical analysis, careful complementary characterization of the studied samples is key – as demonstrated by Ahn et al. in their detective work that settled the controversy over the bandgap value of CZTSe [15]. In this work, we attempt to rectify these oversights, providing much sought-after ellipsometry data determined from device-relevant material. We analyzed ~ 500 nm and ~ 800 nm thick Cu-poor and Zn-rich CZTS absorbers grown on

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bare as well as Mo-coated soda-lime glass (SLG), which yielded solar cells having 2.8% (~500 nm) and 5.3% (~800 nm) solar conversion efficiency, measured on virtually identical samples. The choice of substrates ensures that the as-fabricated CZTS/Mo/SLG absorbers have the same characteristics as those in a device in terms of e.g. grain structure and Na incorporation, while the CZTS/SLG samples offer the possibility to compare the optical absorption coefficients. The composition, structure, phase purity and morphology were carefully examined and the substrate effects were evaluated. Knowledge gained from these characterizations was then used for establishing a realistic optical model for the spectroscopic ellipsometry (SE) analysis, in order to determine the dielectric functions. The SE-derived absorption coefficients were compared with those extracted from complementary spectral transmittance and reflectance measurements done on CZTS/SLG samples.

2. Preparation and characterization

2.1. Preparation

CZTS films were prepared on bare and Mo-coated SLG by DC magnetron reactive co-sputtering of CuS, Zn and Sn targets in Ar and H₂S atmosphere in a Von Ardenne CS600 system, followed by a rapid annealing process [16]. The detailed fabrication procedure can be found elsewhere [17]. Samples pairs S1 (CZTS/Mo/SLG) and S2 (CZTS/SLG) were produced in the precursor-deposition batch A and annealed together in a graphite box. Samples pairs S3 (CZTS/Mo/SLG) and S4 (CZTS/SLG) were produced in the precursor-deposition batch B with longer deposition time to produce thicker films, which were annealed together in a pyrolytic-carbon (Py)-coated graphite box.

2.2. Characterization

2.2.1. Composition by XRF measurements and XPS depth profiling

The composition of the annealed absorber films was determined by X-ray fluorescence (XRF, PANalytical Epsilon 5) measurements. The atomic ratios for the metallic elements were determined to be Cu/Sn=1.82–1.89 and Zn/(Cu+Sn)=0.37–0.47, as shown in Table 1. The samples are Zn-rich with excess Sn even after the Sn-loss caused by the annealing process. Non-stoichiometric samples in such composition range are of great practical relevance as it is well known that Cu-poor and Zn-rich composition prevents the formation of Cu–Sn–S or Cu_xS phases and offer desirable solar cell performances.

The depth-wise distribution of elements in the films was examined using X-ray photoelectron spectroscopy (XPS, Quantum 2000 scanning ESCA Microprobe) depth profiling, in which Al K α radiation was applied as the incident X-ray and an argon ion gun

at an energy of 0.5 keV was applied to sputter atoms away in order to study sample surfaces at different depth. The resulting depth profiles are shown in Fig. 1(a), (b), (c) and (d) for samples S1, S2, S3, and S4, respectively. It can be observed that in the bulk of the film there is no significant variation in elemental distribution of Cu Zn Sn S, whereas toward the front interface of the sample, a trend of Zn enrichment is shared by all samples. The more Zn-rich samples S3 and S4 have different behaviors regarding the locations of Zn-rich zones: S3 shows comparable degree of Zn enrichment at both front (absorber/air) and back (absorber/Mo) interfaces. In contrast, the formation of a Zn-rich zone in sample S4 seems to occur only at the front surface (absorber/air interface). From the Zn surplus observed at the interfaces, ZnS segregations at such regions are to be expected [18–20]. S2 and S4, on SLG substrate, have slightly more Zn segregation at the surface compared to corresponding samples S1 and S3 fabricated on Mo/SLG. This effect may be due to the ample supply of Na by the SLG substrate to S2 and S4, as it was recently found that more Na promotes ZnS precipitation from CZTS grains [21].

2.2.2. Structural and phase examination by XRD and Raman measurements

X-ray diffraction (Siemens D 5000 diffractometer) measurements were done at grazing incidence of 1° with a parallel beam geometry (GIXRD) and Bragg Brentano focusing geometry (θ – 2θ XRD) under the irradiation of CuK α . Fig. 2 shows the diffractograms. The GIXRD diffractograms show that all the samples exhibited strongest peaks at 2θ =28.5° and 47.3°. Both the dominating patterns [22] (solid bars) and the minor peaks [23] (dashed bars) match that of kesterite [22,23]. S1 and S3 also show peaks due to Mo back contact [24]. The peak for S4 at 15° marked with “*” is identified to be that of SnS₂ [25] in both GIXRD and θ – 2θ XRD diffractograms. However, peaks of SnS [26] secondary phases marked with “+” at 31.9° (a combination of two stronger reflections at 31.6° and 32°) and 66.6° are only observed in θ – 2θ XRD for S2 and S4, those with bare SLG substrates. The reasons why SnS_x secondary phases were not observed on S1 and S3 may be explained by their slightly higher Cu/Sn ratio (see Table 1) after the anneal compared to S2 and S4. These results suggest that the CZTS films indeed grow differently on SLG and Mo/SLG, even with otherwise identical fabrication conditions.

Raman spectroscopy was carried out to offer more information regarding the phase purity of the CZTS samples. The measurement was performed in a Renishaw inVia system with laser excitation wavelengths 532 nm and 325 nm with penetration depth ~100 nm and less than ~50 nm, respectively. Fig. 3(a) shows the spectrum recorded when the green laser was applied. All the absorber films share the same features that are typically expected from kesterite CZTS with two main Raman modes appearing at 287 cm⁻¹ and 335–338 cm⁻¹ and weaker Raman modes appearing at 166 cm⁻¹, 350 cm⁻¹, 374 cm⁻¹. Minor modes marked as

Table 1

Compositional and structural data for the CZTS absorber films. The tabulated device performances V_{oc} , J_{sc} , FF, η are the open circuit voltage, short circuit current, fill factor and power conversion efficiency measured on virtually identical samples to S1 and S3. Device parameters in brackets are from the best cell in each case. More details of the device measurements can be found in the “Supplementary materials”.

Sample ID	Fabrication batch; Graphite box	XRF Cu/Sn	XRF Zn/(Cu+Sn)	AFM σ_{RMS} (nm)	SEM Thickness (nm) CZTS	MoS _x	Device performance of average cell (best cell)
S1 CZTS/Mo/SLG	Batch A Uncoated box	1.87	0.37	27.7	503 ± 36	98 ± 13	V_{oc} (mV)=444 (478); J_{sc} (mA/cm ²)=13.6 (13.3); FF(%)=46 (46.6); η (%)=2.8 (3.0).
S2 CZTS/SLG	Batch A Uncoated box	1.82	0.39	53.9	520 ± 57	–	–
S3 CZTS/Mo/SLG	Batch B Py-coated box	1.89	0.47	22.7	797 ± 28	136 ± 12	V_{oc} (mV)=584 (607); J_{sc} (mA/cm ²)=17.1 (17.1); FF(%)=52.6 (56); η (%)=5.3(5.8).
S4 CZTS/SLG	Batch B Py-coated box	1.87	0.46	30.6	783 ± 37	–	–

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