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Cu_2ZnSnS_4 thin film solar cells grown by fast thermal evaporation and thermal treatment

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ABSTRACT

Cu_2ZnSnS_4 thin films have been produced via rapid thermal evaporation of off-stoichiometric kesterite powder followed by annealing in an Ar atmosphere. Different heating rates were applied during the thermal treatments. The chemical composition and structural properties of the deposited layers as well as the distribution of the elements through the kesterite thin film have been investigated. The initial growth of a SnS secondary phase during evaporation led to the formation of this secondary phase next to the Mo back contact. Solar cell power conversion efficiencies were limited to values about 3% due to this secondary phase. Furthermore, an increased open circuit voltage was demonstrated by using a Zn(O,S) buffer layer.

1. Introduction

Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSnSe_4$ (CZTSe) and $Cu_2ZnSn(S,Se)_4$ (CZTSSe) kesterite materials are promising alternatives to Cu(In,Ga)Se_2 for photovoltaic applications. These materials are characterized by a high absorption coefficient and direct band gap energy in the range of 1.0–1.5 eV. Additionally, these kesterite materials are composed by low cost and abundant elements relative to indium (Mitzi et al., 2011). Despite these properties, a maximum power conversion efficiency of 12.6% has been achieved for CZTSSe devices (Wang et al., 2014), which is notably below the 22.6% achieved for Cu(In,Ga)Se_2 solar cells (www.pv-magazine.com).

The main limitation of kesterite solar cells is the open circuit voltage (V_{oc}) deficit relative to the absorber band gap energy (E_g) (Liu et al., 2016). Different reasons for the large V_{oc} deficit (around 840 mV for CZTS) have been proposed. One reason that can explain the reduced V_{oc} is an unfavorable alignment of the conduction band minimum (CBM) at the CZTS/CdS interface. CdS has a lower CBM compared to CZTS, resulting in a "cliff" type of interface, which will lead to enhanced interface recombination. The use of $Zn_{1-x}Cd_xO_y$ buffer layer deposited by atomic layer deposition (ALD) instead of CdS has led to an increased in V_{oc} and device performance (Plätzer-Björkman et al., 2015). Another reason for the large V_{oc} deficit can be the non-optimal bulk quality of the kesterite absorber and the presence of secondary phases (Siebentritt and Schorr, 2012), such as SnS with lower E_g (Xie et al., 2014). A Cu-poor/Zn-rich composition seems to be ideal to achieve high performance CZTSSe devices (Fairbrother et al., 2015). This off-stoichiometry can result in the formation of ZnS(Se) secondary phase, which can block the current flow and introduce dead areas in the cell (Siebentritt and Schorr, 2012). Moreover, the existence of large spatial band gap fluctuations coming from high concentrations of Cu-Zn antisite disorder can also contribute to the V_{oc} deficit (Scragg et al., 2016). The formation energy of defects is determined not only by the composition, but also by the growth parameters (temperature and pressure) of the absorber layer (Liu et al., 2016). Variations in processing conditions affect the kesterite phase formation, and hence the solar cell devices performance. Many processing conditions and methods have been reported to grow quality kesterite films. CZTSSe solar cells fabricated by a hydrazine-based non-vacuum process exhibit a maximum power conversion efficiency of 12.6% (Wang et al., 2014). Alternatively, 9.1% was achieved for a pure CZTS absorber layer fabricated by annealing of a glass/Mo/ZnS/Sn/Cu/ZnS precursor stack in H_2S balanced with N_2 (Tajima et al., 2014; Fukano et al., 2013). Chemical routes have the advantage of reducing processing costs of the technology and have produced the best kesterite solar cells this far.

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Generally, vacuum-growth processes can lead to higher reproducibility and high quality semiconductor materials; however a higher processing cost is typically required.

The objective of this work is to grow quality CZTS thin films for efficient solar cells by fast evaporation technique. CZTS layers have been deposited by thermal evaporation of off-stoichiometric CZTS in only 12 min followed by annealing in Ar atmosphere, considerably reducing the synthesis time of kesterites. Up to our knowledge, this is the first time that kesterite thin film solar cells are produced by fast evaporation of the absorber layer. The effect of the heating rate in the thermal treatment on the properties of the kesterite absorber and solar cell devices is investigated. In addition, an attempt to increase V_{oc} was carried out by the use of a Zn(O,S) alternative buffer layer.

2. Experimental details

2.1. Deposition of Cu_2ZnSnS_4 thin films

For the evaporation source, a Cu-rich/S-poor Cu_2ZnSnS_4 compound was synthesized by solid state reaction (Valle-Rios et al., 2016). CZTS thin films were fabricated by a two-stage process. In the first stage, CZTS thin films were deposited by thermal evaporation onto Mo coated glass using the precursor compound in powder form. CZTS powder was placed in a molybdenum crucible. The deposition rate was controlled by gradually increasing the current through the crucible, avoiding any spitting effect, and was monitored by a quartz crystal balance. Substrates were heated to nominal temperature of 250 °C. CZTS thin films with a thickness of 1.5 μm were evaporated in only 12 min. The second stage of the process consisted of a thermal treatment of the samples at 550 °C in Ar atmosphere at a pressure of 9.5×10^4 Pa under excess sulfur. For that purpose, the as-evaporated thin films were placed in a partially closed graphite box of 56 mm × 70 mm × 20.5 mm with a hole of 1 mm diameter in the lid, and inserted into a quartz tube furnace (Caballero et al., 2015). In order to have an overpressure of sulfur, 120 mg of pure elemental sulfur (99.999%) were added to the graphite container. Heating rates of 2 °C/min, 5 °C/min, 10 °C/min were used with cooling rate of 10 °C/min in all cases. TT1, TT2 and TT3 refers to the thermal treatment with heating rates of 2 °C/min, 5 °C/min and 10 °C/min, respectively. Here, the influence of the heating rate on the CZTS thin film properties was investigated. Table 1 summarizes the different thermal treatments carried out and the composition of the thin films and bulk compound.

2.2. Device fabrication

Solar cells with the CZTS absorber layers annealed at different heating rates were fabricated by using a CdS buffer layer deposited by chemical bath deposition. Two types of window layers were employed. In the first case, 50 nm of i-ZnO and 350 nm of In_2O_3:SnO_2 (ITO) were deposited by DC-pulsed sputtering to act as a transparent conductive window layer. In this case, the absorber layer was etched with $(NH_4)_2S$ before the buffer layer deposition (Xie et al., 2014). In the second configuration, the window layer consisted of an i-ZnO/ZnO:Al (AZO) bilayer deposited by sputter deposition and Ni-Al grids were grown by thermal evaporation to enhance the current collection. In this last configuration, KCN etching was carried out before CdS deposition with the objective of cleaning the absorber surface and removing the possible oxides formed (Lehmann et al., 2014). Moreover, an alternative buffer layer of Zn(O,S) was deposited by RF-sputtering, being the structure of the solar cell: glass/Mo/CZTS/Zn(O,S)/ZnO:Al/Ni-Al (Klenk et al., 2014). KCN etching was also performed before this alternative buffer layer. Table 2 shows photovoltaic parameters for solar cells fabricated from the described configurations.

2.3. Characterization techniques

The chemical composition was measured by energy dispersive X-ray spectroscopy (EDX) (Oxford instruments, model INCAx-sight) inside a Hitachi S-3000N scanning electron microscope (SEM). EDX measurements were carried out at 25 kV operating voltage, and the Cu-K, Zn-K, Ge-K, Sn-L and S-K lines were used for quantification. Grazing incidence X-ray diffraction (GIXRD) was performed to investigate the structural properties of the CZTS thin films. GIXRD data were collected with a PANAlytical X'Pert Pro MPD diffractometer, using Cu K_α radiation and a multilayer mirror to produce a parallel beam. Detector scans with grazing incident angles (GI) of 0.5°, 1° and 3° were carried out. Glow discharge optical emission spectroscopy (GDOES) with a Spectruma GDA 650 was performed in pulsed RF mode to study the elemental profile through the whole CdS/CZTS/Mo layer. Argon plasma with a pulsed RF mode was used to sputter the CdS, CZTS and Mo layer and the ionized atoms from the layer are detected with a CCD array. Micro-Raman spectra were obtained at 21 °C in a Horiba Jobin Ivon T64000 spectrometer. The laser wavelength was adjusted to 633 nm and 325 nm with a spot size of 1.25 μm diameter.

I-V characteristics were measured using a Sun 3000 class solar simulator (Abet Technologies Inc., Milford, Connecticut, USA). Measurements were carried out at 25 °C and under air mass AM1.5 with 100 mW/cm^2 illumination. External quantum efficiency (EQE) and internal (IQE) measurements were performed using a Bentham PVE300 system (Bentham Instruments Ltd., Berkshire, UK) calibrated with a Si and Ge photodiode. Reversed voltage-biased EQE curves were collected by connecting a Keithley 2400 source meter (Keithley Instruments Inc., Cleveland, Ohio, USA) directly to the primary coil of the transformer and biasing the device at the desired voltage.

Table 1
Thermal treatments and composition of the bulk and thin films.

Sample	Thermal treatment	Cu (at%)	Zn (at%)	Sn (at%)	S (at%)	Cu/(Zn + Sn)	Zn/Sn	S/M
Precursor	–	27.27	14.39	15.81	42.53	0.90	0.91	0.74
As-evap.	–	28.85	13.54	14.37	43.25	1.03	0.94	0.76
R7_TT1	2 °C/min	20.68	11.84	16.08	51.40	0.74	0.74	1.06
	2 °C/min + $(NH_4)_2S$	21.12	12.38	14.31	52.19	0.79	0.87	1.09
R7_TT2	5 °C/min	20.82	11.71	16.19	51.29	0.75	0.72	1.05
	5 °C/min + $(NH_4)_2S$	22.51	12.79	14.71	49.99	0.82	0.87	1.00
R7_TT3	10 °C/min	20.82	11.33	15.35	52.5	0.78	0.74	1.11
	10 °C/min + $(NH_4)_2S$	22.21	12.14	14.68	50.97	0.83	0.83	1.04

Note: All the thermal treatments were carried out at 550 °C for 1 h.