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Relevant efficiency enhancement of emerging Cu_2MnSnS_4 thin film solar cells by low temperature annealing

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ABSTRACT

Earth abundant and low cost Cu_2MnSnS_4 (CMTS) thin films were grown by a two-step vacuum approach: metal precursor stacks grown by thermal evaporation were heat treated in elemental sulfur vapors. Cu-poor/Mn-rich CMTS samples with large grain size and good layer compactness were obtained by sulfurization at 585 °C with an initial step at 115 °C to enhance the metal intermixing. They were primarily tested by Energy Dispersive Spectroscopy, micro-Raman and Photoluminescence. Then, solar cells based on them were realized and tested, showing enhanced performance with respect to a previous study (efficiency 0.5%, open-circuit voltage 302 mV, short-circuit current density 4.6 mA/cm^2, fill factor 36%). A 40 min post-deposition annealing in air at 225 °C significantly improved the performance of these emerging PV devices (efficiency 0.83%, open-circuit voltage 354 mV, short-circuit current density 5.8 mA/cm^2, fill factor 40%). The beneficial effects of the low temperature annealing were investigated, in terms both of material properties and PV device performance modification.

1. Introduction

As it is well known, in the last five years thin film solar cell manufacturers strongly suffered from the abrupt decrease of Si module price well below 1$/W$_p$ (Bermudez, 2017). The attention of the research activity on thin film photovoltaics (PV) was therefore even more focused on high efficiency or very low cost materials. Despite the present efficiency of Cu(In, Ga)Se_2 (CIGS) thin film solar cells is almost comparable to the well established PV technology based on silicon (Jackson et al., 2011; Poncelet et al., 2017), the low availability in the Earth crust of indium and gallium will lead to a progressive increase of their cost, which is expected to constrain terawatt range applications of CIGS-based PV devices (Tao et al., 2011). An attractive alternative for the synthesis of In and Ga free terawatt-scale chalcogenides relies on I_2-II-IV-VI_4 species, such as copper zinc tin sulfide (CZTS), copper zinc tin selenide (CZTSe) and the sulfur-selenium alloy (CZTSSe) (Suryawanshi et al., 2013; Tombolato et al., 2015). A further compound belonging to this class of materials is copper manganese tin sulfide (CMTS), a p-type semiconductor fully based on Earth-abundant and low-cost elements. As a matter of fact, since Mn is definitely cheaper than Zn, optimized CMTS could potentially provide W$_p$ cost definitely lower than CZTS, which is crucial for thin film PV applications (Marchionna et al., 2017). CMTS, which crystallizes into a stannite structure (space group: I-42m), shows high absorption coefficient ($\cong 10^4$ cm^{-1}) and direct band gap (Liang et al., 2012; Cui et al., 2012) suitable for PV applications. So far, CMTS was mainly studied as magnetic semiconductor in the form of single crystal or nanocrystal (Liang et al., 2012; Cui et al., 2012; Fries et al., 1997; Podsiadlo et al., 2015), while, very recently, few papers reported on CMTS thin films for PV applications (Marchionna et al., 2017; Chen et al., 2015a,b, 2016). In Chen et al. (2015a) the synthesis and properties of CMTS layers prepared by direct liquid coating followed by annealing in nitrogen atmosphere were described, which were used in Chen et al. (2015b) as PV absorbers in solar cells with 0.49% maximum efficiency. Some of the same authors reported also on CMTS PV absorbers prepared by direct liquid coating followed both by annealing in nitrogen atmosphere and post-sulfurization in sulfur vapors, reaching a 0.38% maximum efficiency (Chen et al., 2016).

In this work, CMTS thin films were grown by a two-step process, whose first optimization is reported in Marchionna et al. (2017). Metal precursor stacks grown by thermal evaporation are annealed in non toxic sulfur vapors. As it is widely known, this deposition approach led to record efficiency both in CIGS (Jackson et al., 2011) and pure sulfide CZTS (Shin et al., 2013). Of the many possible stoichiometries, Cu-poor/Mn-rich CMTS films

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with Mn/Sn ratio around 1 were chosen in order to prevent the development of both highly conductive (e.g. $Cu_{2-x}S$) and insulating (e.g. MnS) secondary phases. The grown CMTS thin films were tested by Energy Dispersive Spectroscopy, Raman and Photoluminescence, then some solar devices were manufactured and tested, as described in the following. Considering the beneficial effects of low temperature post-deposition annealing either in air or inert atmosphere recently reported in the literature for kesterite based solar cells (Neuschitzer et al., 2015; Jiang et al., 2016), the effect of thermal treatments between 200 and 275 °C on CMTS solar cell efficiency was investigated, both in terms of electrical performance and modification of the material properties. The results are reported and discussed.

2. Experimental

CMTS thin films with approximate final thickness around 1.5 μm (measured by a Veeco-Dektak 150 profilometer) were grown by a two step process. Metal precursors were deposited by thermal evaporation on $4 \times 4\ cm^2$ Mo coated soda lime glasses (SLG) in the sequence SLG/Mo/Sn(235 nm)/Cu(176 nm)/Mn (135 nm). The Mo back contact deposited by DC magnetron sputtering was 1 μm thick. All metal precursor layers have been deposited by a 4-sources electron beam (EB) evaporation system (Kurt J. Lesker PVD 75) in a high vacuum chamber with 2×10^{-7} mbar base pressure. Both Sn and Cu beads were evaporated with deposition rates of 2.5 Å/s and 1.5 Å/s, respectively, while Mn powders were evaporated at 3 Å/s.

CMTS thin films were then formed by thermal treatment of the metal precursors in sulfur vapors. Such a sulfurization process was performed in a tube furnace, where the stack of metal precursors and a quartz crucible with 0.3 g of sulfur were loaded in the same quartz boat. The metal precursors were then annealed at 585 °C in a mixed argon ($50\ cm^3$/min flux) and elemental sulfur atmosphere for 60 min (ramping rate of 15 °C/min), with an additional initial step at 115 °C for 60 min, to enhance the metal intermixing.

Both morphology and chemical composition of the CMTS layers were investigated by a MIRA3 Tescan Scanning Electron Microscope (SEM) equipped for Energy-Dispersive Spectroscopy (EDS). The operating voltage used for all the SEM images was 20 kV, while EDS analyses were performed by a Quantax system (Bruker) under the following conditions: operating voltage 20 kV, probe current 150 pA, probe size 5 nm, working distance 15 mm, with inner-calibration on pure metals.

The crystal structure of the CMTS films was examined by Raman spectroscopy. Raman measurements were carried out at room temperature by a Jasco Ventuno micro-Raman system in backscattering configuration, equipped with a Peltier-cooled charge-coupled device camera (operating temperature: −50 °C) and a He-Ne laser (excitation wavelength: 632.8 nm). Raman spectra were calibrated before each measurement by imposing the position of the dominant peak of a monocrystalline Si reference at $520.65\ cm^{-1}$. Proper laser power density was chosen to generate the best signal-to-noise ratio without broadening or shifting the Raman peaks due to local heating. In particular, a 20X-0.46 NA objective providing a spot diameter of 4 μm and a laser power of 0.8 mW were used.

Photoluminescence (PL) spectra were recorded both in the 450–800 nm and in the 850–1700 nm spectral range. PL measurements in the visible range were performed with a spectral resolution of 5 nm by a Fluorolog 3.21 spectrometer provided by Jobin Yvon. The excitation source consists of a 450 W Xe lamp coupled with a 1200 grooves/mm double grating monochromator. The signal detection equipment consists of a 1200 grooves/mm single grating monochromator and of a phototube detector (Hamamatsu R928P). A cooling system consisting of rotary pump, diffusion pump, l-N_2 cold trap and Cryomech PT405 cryorefrigerator was used to perform PL measurements at low temperature up to 7 K. As far as analyses in the IR range are concerned, PL measurements were performed with a spectral resolution of 6.6 nm using a standard lock-in technique in conjunction with a single grating monochromator and a short wavelength enhanced InGaAs detector with maximum responsivity at 1540 nm. A quantum well laser (λ_{exc} = 805 nm) was mainly used as excitation source, along with a 532 nm laser sometimes employed for comparison purposes. A cooling system consisting of rotary pump, turbomolecular pump and He closed circuit cryostat was used to perform PL measurements at low temperature up to 15 K.

CMTS solar cells with an active area of $0.15\ cm^2$ were then obtained as reported in Marchionna et al. (2017).

Post-deposition thermal treatments in air or Argon atmosphere at 200, 225, 250 and 275 °C for 10–120 min were finally tested to investigate the effect of low temperature annealing on CMTS solar cell efficiency. Despite in the literature hot plates in open air were usually employed to this purpose (Neuschitzer et al., 2015; Jiang et al., 2016), in this work a pre-heated lab drying oven was preferred to perform thermal treatments in air. In fact, lab drying ovens provide homogeneous heating and ensure temperature stability and reproducibility, thus minimizing the time needed to heat the CMTS solar cells up to the chosen temperature. Annealing in Argon atmosphere was instead performed using a quartz tube and a pre-heated tube furnace. In both cases, the samples were removed from the pre-heated environment at the end of the annealing time and cooled down to room temperature in a couple of minutes.

The CMTS devices were inspected both by External Quantum Efficiency and current density-voltage (J-V) measurements before and after each annealing. External Quantum Efficiency (EQE) measurements were obtained by a SpeQuest quantum efficiency system. The PV devices were illuminated by a chopped light beam with a diameter around 3 mm. The photogenerated current from the cell passed through an I-V converter and the corresponding voltage produced at each wavelength of the monochromatic light was measured by a lock-in amplifier monitored via PC. The spectral response curves of the PV device were taken from 350 nm to 1200 nm with a 10 nm wavelength increment. The EQE spectrum was then calculated as the ratio between the spectral response data and the incident light spectrum, obtained by a reference photodiode (ThorLabs S120VC). J-V measurements under 1 Sun illumination ($100\ mW/cm^2$) in Air Mass 1.5G conditions were recorded by a Thermo Oriel Solar simulator.

3. Results and discussion

As pointed out in Marchionna et al. (2017), the strict control of the Mn deposition rate is a critical issue, since in the selected operative conditions Mn sublimates at very low EB current. Despite in Marchionna et al. (2017) SLG/Mo/Mn/Sn/Cu/Mn stack structures led to the best CMTS morphology, in this work metal precursors were grown in the sequence SLG/Mo/Sn/Cu/Mn. As a matter of fact, a two-step Mn evaporation increases the error on the total Mn thickness, which in turn negatively affects both the sample reproducibility and the solar cell performance due to a higher content of the $Cu_{7.38(11)}Mn_4Sn_{12}S_{32}$ insulating secondary phase, as demonstrated in Marchionna et al. (2017). Furthermore, Mn powders were used for the Mn evaporation, as an alternative to the Mn flakes employed in Marchionna et al. (2017), which also enhanced the control on the final Mn layer thickness. The effectiveness of these simple modifications to the previous optimization (Marchionna et al., 2017) is proven first of all by EDS analyses