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Influence of silver incorporation on CZTSSe solar cells grown by spray pyrolysis

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ABSTRACT

Chemical spray pyrolysis was employed to prepare kesterite Cu_2ZnSnS_4 layers with different Ag contents. The Cu_2ZnSnS_4 layers were processed at 350 °C from solutions of Cu, Ag, Zn and Sn metal salts and thiourea dissolved in water as the most environmentally friendly solvent. The as-prepared layers were subsequently annealed at high temperature in chalcogen atmosphere in order to obtain well crystallized kesterite $Cu_2ZnSn(S,Se)_4$ absorber layers. The influence of different Ag contents on the properties of the as-prepared layers, the resulting absorbers as well as the devices performance was investigated.

Enhanced crystallinity and grain growth were observed for Ag containing as-prepared layers as well as selenized layers. As a potential consequence, this enhanced grain growth appears to facilitate the formation of $MoSe_2$ layer at the back contact/absorber interface during the selenization process. Further, the incorporation of Ag improved the performance of kesterite devices up to 7.1% for 5% Ag/(Cu + Ag) composition. However, for Ag contents beyond this level we observed impairing of the device efficiencies with higher Ag content.

1. Introduction

Kesterite compounds have gained interest in the last decade as promising earth abundant absorber materials for thin film solar cells [1,2]. The efficiency of the kesterite devices has stagnated at efficiencies lower than 13% [3–6] in the last few years, which is much lower than the predicted value from the Shockley-Queisser limit [7,8].

Many reports have assigned the poor performance of the kesterite devices to the low open circuit voltage (V_{OC}) or to the large V_{OC} deficit, relative to the respective band gap, which is a major barrier in reaching higher efficiencies [9,10]. Although the origin of the V_{OC} deficit in kesterite solar cells is still unclear, a not adequately optimized interface at the front contact and the high density of bulk defects can be reasonable origins for the V_{OC} deficit [11,12].

Further improvement of solar cell efficiency relies on handling the challenges of better understanding of the material properties and device physics and hence reducing this large V_{OC} deficit.

Several approaches have been adapted to reduce the V_{OC} deficit, namely, reducing the high density of bulk defects and reducing the interface recombination loss [13]. Modifications of the back- and front contact interfaces have been employed to reduce the interface recombination and improve the V_{OC} [14].

Various barrier layers, such as TiN [15,16], CuGe [17], TiB_2 [18] and ZnO [19] at the back contact/kesterite interface have been assessed in order to suppress the formation of $MoS(e)_2$ and the possible decomposition reaction at the back contact interface during the annealing process and hence improve the crystal quality of the absorber and reduce the back contact interface recombination. Moreover, alternative buffer layers, such as $Zn_{1-x}Cd_xS$ [20], $Zn_{1-x}Sn_xO_y$ [21] and a hybrid CdS/In_2S_3 [6] have been investigated with the aim to optimize the front contact interface.

Also, partial substitution of the elements of the $Cu_2ZnSn(S,Se)_4$ (CZTSSe) crystal has recently been the center of interest in order to tune the band gap, reduce the bulk defects and enhance the quality of the absorber layer. Band gap grading in CZTSSe absorber layer, utilizing varied S/Se content within the absorber layer, led to the lowest reported V_{OC} deficit and a CZTSSe device with efficiency of 12.3% was obtained, which is the highest efficiency from vacuum processed kesterite solar cells [4].

Cation substitution with elements of larger atomic size serves as a way to effectively modify the optoelectronic properties of the CZTSSe structure. Many reports have shown improved device performance from partial substitution of Sn with Ge [22–24] and substitution of Zn with Cd [25,26].

Further studies focused on inhibiting Cu_{Zn} and Zn_{Cu} anti-site defects, which cause cationic disorder in the kesterite lattice associated with band tail states within the absorber band gap [27,28].

Ag is an appealing candidate for substitution of Cu, as it can

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improve the quality of the absorber as well as the device performance. Gong et al. [29] investigated the crystal structures and the optical properties of $(Ag_x,Cu_{1-x})_2ZnSnS_4$ (ACZTS) and $(Ag_x,Cu_{1-x})_2ZnSnSe_4$ (ACZTSe) solid solutions. The energy band gap decreased with Ag content lower than 20% and increased for higher Ag content.

Hages et al. [30], Guchhait et al. [31] and Gershon *et. al.* [32] reported the beneficial effect of low Ag content (i.e. 5%, 7% and 10%, respectively) on the absorber grain growth, defects density and device performance. Nanocrystal-based ACZTSe with 5% Ag showed enhanced grain growth, reduced band tailing and better device performance. However, ACZTSe with 50% Ag showed poor device performance, despite the improved optoelectronic properties of the absorber relative to 5% ACZTSe and CZTSe [30]. Spin coated CZTS layers with low Ag content (< 7 mol% of the Cu content) showed similar enhancement in the overall performance of CZTS solar cells [31]. In the case of co-evaporated ACZTSe only ≈ 10% Ag could be demonstrated to improve the device efficiency [32]. Thus, according to these reports, the relevant range for Ag admixture appears to be around 5–10%, whereas the optimum value depends on the fabrication method.

Only a few studies have been reported to indicate how Ag substitution impacts the fundamental properties of the as-prepared layers, selenized absorbers as well as the device performance.

Moreover, the low cost chemical spray pyrolysis was used to deposit Cu_2ZnSnS_4 (CZTS) layers using different atomization procedures, such as ultrasonic atomization [33] and pneumatic atomization [34]. Hillhouse et al. reported the highest kesterite device efficiency of 11% obtained from ultrasonic spray pyrolysis with Ge alloying [35], however using hazardous dimethylformamide as a solvent is one main drawback of this approach, due to its potential toxicity. Solar cells obtained from the much simpler pneumatic spray pyrolysis did not achieve high efficiency so far; nevertheless, a few studies reported efficiencies around 5% using water based solution [36,37], which is more convenient as water is the safest and the most environmentally friendly solvent.

In this study, simple pneumatic spray pyrolysis was employed to prepare CZTS layers with different Ag contents. The structural and morphological properties of the as-prepared and the selenized layers were investigated. Furthermore, CZTSSe solar cells were processed and efficiency of 7.1% is demonstrated.

2. Experimental details

CZTS layers were deposited onto the pre-heated Mo-coated soda lime glass (SLG) substrates with different Ag contents using a home-built chemical spray pyrolysis setup. The spray solution was prepared with 5.7 mmol silver nitrate ($Ag(NO_3)_2$, Carl Roth), 5.7 mmol copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$, Sigma Aldrich), 4.3 mmol zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, Sigma Aldrich), 3.7 mmol tin methanesulfonate ($Sn(CH_3SO_3)_2$, Sigma Aldrich) and 40 mmol thiourea ($SC(NH_2)_2$, Sigma Aldrich). All used salts were dissolved in distilled water separately and mixed together before spraying. Sulfur composition in excess was taken to compensate the possible sulfur loss and to restrain the formation of oxides during the spraying process. The pH value of the spray solution was adjusted to around 2 by adding a few drops of concentrated nitric acid. The selected compositions were chosen to yield Cu-poor and Zn-rich absorbers after annealing. To investigate the influence of Ag on the properties of the layers, the Ag concentration was varied in the spray solution in order to obtain CZTS layers with different Ag contents. Four samples were prepared with nominally $Ag/(Ag + Cu) = 0\%$, 5%, 10% and 15% in the spray solution. The obtained samples were labelled as 0Ag, 5Ag, 10Ag and 15Ag.

The prepared solution was sprayed using a solution flow rate of $250\ \mu L\ min^{-1}$ onto the pre-heated SLG/Mo substrate. The substrate temperature was maintained constant at 350 °C during the spray process. Nitrogen at 1.5 bars was used to atomize the solution into a fume of fine droplets and to transport it onto the pre-heated substrate. The spraying duration was 15 min for all prepared samples.

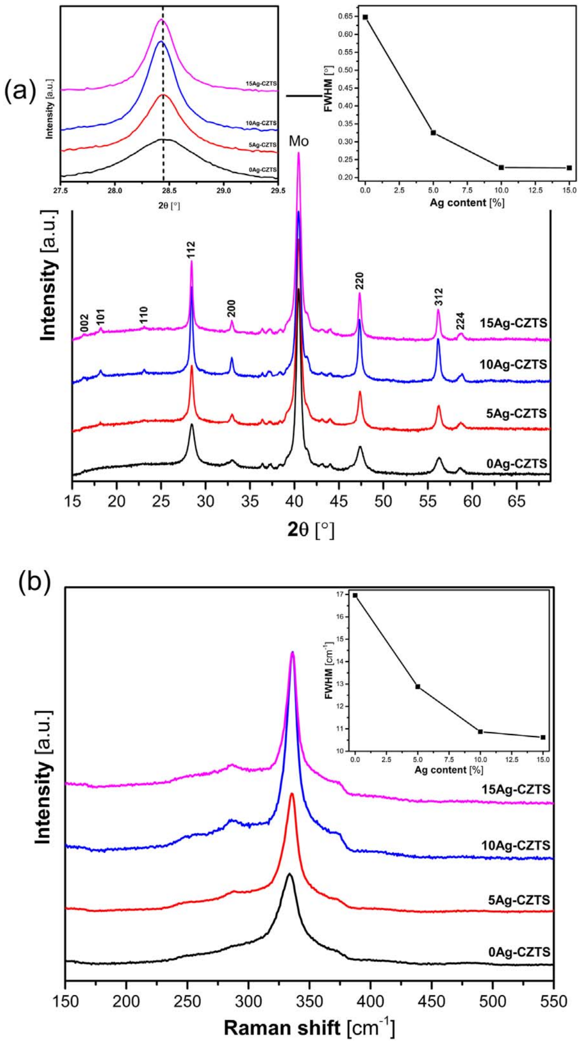

Fig. 1. (a) X-ray diffraction (XRD) patterns and (b) Raman Spectra of as-prepared CZTS layers with different Ag contents.

The CZTS layers were afterward selenized in a rapid thermal processor (RTP) (ANNEALSYS As-One 150). The samples were placed inside a graphite susceptor containing selenium pellets (MaTech, 99.999%) and SnSe crystals (Alfa Aesar, 99.999%) and annealed at 530 °C for 8 min, the heating ramp was 120 °C/min and the cooling was done by switching off the heater.

Structural properties of the as-prepared CZTS layers and selenized CZTSSe layers were analyzed by X-ray diffraction (Panalytical X′pert Pro diffractometer with a CuKα radiation at 40 kV and 40 mA) and Raman spectroscopy (Raman, Horiba LabRAM Aramis) equipped with a green laser with an excitation wavelength of 532 nm and a blue laser with an excitation wavelength of 457.9 nm, which is especially sensitive for ZnSe [38], both at a laser power of 3 mW and a spot size of approximately 1 μm. The top surface and cross section morphology of the CZTSSe layers were characterized by scanning electron microscopy (FEI Helios Nanolab 600i SEM/FIB).

All selenized samples were processed to complete devices by further deposition of CdS as buffer layer and i-ZnO/ZnO:Al as window layer. The CdS layer was deposited on the CZTSSe layers using chemical bath deposition, the thickness amounts to 60 nm. Then, the device was completed by subsequent deposition of 75 nm i-ZnO and 350 nm ZnO:Al layers via RF sputtering. No further processing steps were made.

Current–voltage (*I–V*) and Capacitance–voltage (*C–V*) measurements were performed for electrical characterization of the devices. The

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