



Easy and low-cost aqueous precipitation method to obtain $\text{Cu}_2\text{ZnSn}(\text{S}, \text{Se})_4$ thin layers



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ABSTRACT

An easy method to obtain kesterite $\text{Cu}_2\text{ZnSn}(\text{Se}_{1-x}\text{S}_x)_4$ (CZTSSe) thin films as absorbers for photovoltaic solar cells is discussed in this report. Particular emphasis is directed towards preparation steps of CZTSSe, as well as its crystal structure and properties. The CZTSSe has been developed by a low-cost and sustainable aqueous precipitation method that included metal selenite's precipitation, its reduction to metal selenides and further crystallization of kesterite. The use of an aqueous solution instead of organic compounds and sulfurization process at atmospheric conditions makes this process attractive for large-scale industrial fabrication of CZTSSe thin film solar cells.

The kesterite CZTSSe solid solution has been characterized in terms of its chemical composition, structural and morphological transformations and optical and electrical properties, confirming the viability and effectiveness of the applied process. The optimal electrical parameters were found to be: 21.5 mA/cm² short circuit current (Jsc), 532 mV open circuit voltage (Voc), 42.8% fill factor (FF) and total area efficiency of 4.9% (Eff) without antireflection coating.

1. Introduction

Thin film solar cells, based on CIGS ($\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$) absorber compound, are noteworthy, reaching great efficiencies [1]. They are considered as one of the most promising thin-film solar cells, and have recently seen growing commercial success. However, high production costs originating from vacuum techniques employed to obtain the films and rare element (gallium and indium) content make this material undesirable for future industrial applications [2]. In contrast, solar cells based on CZTSSe are an attractive and well-suited substitute to CIGS due to their sustainable and low-cost production. In addition, this compound exhibits an optimal and easily adjustable band gap that ranges between 1.1 and 1.5 eV [3] and a large absorption coefficient ($> 10^4 \text{ cm}^{-1}$).

Kesterite absorber layer presents several problems during its preparation such as: volatility of certain compounds (e.g $\text{Sn}(\text{S}, \text{Se})_2$) [4] during the quaternary structure formation, phase decomposition into binary compounds under reaction conditions [5,6] and simultaneous formation of binary and ternary chalcogenide compounds (e.g. $\text{Zn}(\text{S}, \text{Se})$, $\text{CuSn}(\text{S}, \text{Se})_3$) [7,8]. Observed drawbacks for getting a single-phase material, through non-vacuum methods, have stimulated research on different preparation routes that could address these shortcomings.

An outstanding method of preparation is a Precursor-Solution Direct Deposition (PSDD) route. It is based on a direct formation of kesterite layers after thermal treatment. This pure solution approach offers precursors homogeneity at a molecular or atomic scale enabling a precise stoichiometric control. In addition, this route achieves excellent film consistencies, which are necessary for low-cost and large-scale production. World-record kesterite solar cell with 12.6% efficiency has been developed by a PSDD method using a hydrazine-based ink [9,10]. This ink is highly toxic and unstable. It also requires special conditions and storage equipment, which make this procedure unsuitable for industrial applications. To avoid these drawbacks, many other hydrazine-free preparation routes have been already tested. Low-toxicity organic solvents such as alcohols [11,12], amines [13] and dimethyl sulfoxide (DMSO) [14], have been used for direct deposition of the absorber layers. Using DMSO as the solvent, an efficiency of near of 10% was attained [15]. A mixture of water and ethanol was also employed with an efficiency result of 6.2% [16].

Another important chemical method to obtain kesterite films is through a particle synthesis method. It consists of the development of a powder which is later dispersed and deposited over a substrate. Then the substrate is annealed in order to obtain high-crystallinity kesterite

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layers. A sol-gel route could be considered as a possible example of this method. It is based on xerogels formation followed by multiple annealing and treatment steps [17–20]. Recently, films grown by an improved sol-gel method were used to demonstrate a cell with an efficiency of 8.2% [21]. Surfaces with uniform morphology have been obtained via colloidal sol spin-coated layers which reach the desired kesterite phase after several pre-annealing steps (12 times) and a thermal treatment. In this method, the applied solvent (2-methoxyethanol) is highly toxic. In addition, the preparation time (24 h) of precursor solution and numerous annealing steps (12) would pose difficulties in a possible industrial application.

The hot-injection (H-I) route [17–21] had also reached an efficiency over 9% [22]. Some drawbacks related to the difficult-to-clean solvents (e.g. oleylamine), expensive reagents (e.g. acetylacetonates) or vacuum steps increase the total costs of manufacturing. Other routes as solvothermal [17,23,24], rotatory ball milling [25], microwave [26], or non-injection methods [27] are being developed but they have not yet achieved significant performances yet. A sprayed-particle route has obtained remarkable efficiency of 10.8% [28] and it is a relatively attractive way of preparation due to the low-cost reagents (metal chlorides) and solvents (water and ethanol) and an easily scalable deposition technique (spray deposition). Perhaps, a disadvantage may be the fact that most reaction steps required closed atmosphere in presence of N_2 .

In general, the chemical methods are promising ways for CZTSSe preparation due to their efficient material use, safety and high throughput [29]. However, most of these methods show disadvantages in terms of cost, toxicity and re-sizing which hinder the transfer of knowledge from the laboratory to large-scale production.

In this aspect, we are reporting a method of preparation that could be of important commercial interest due to its simplicity. We are using water as a solvent and a precipitation mixture that is easily deposited by Doctor Blade technique onto a substrate. Water is non-toxic, non-expensive and non-reactive in air. Thus, we don't have the difficulty of removing organic compounds. In addition, a sulfurization process at atmospheric pressure is applied to crystallize the desired $Cu_2ZnSn(Se_{1-x}S_x)_4$ phase avoiding the use of elemental selenium in the furnace during treatment. Working at atmospheric conditions makes this route easier and cheaper than other processes that need an inert atmosphere such as spray method [28] or hot-injection [22]. Only few syntheses using water in combination with organic compounds have been reported for particle routes [28,30–32].

2. Experimental

2.1. Synthesis of precursors

The reagents used for the synthesis were $Cu(NO_3)_2 \cdot 3H_2O$ (99%, Aldrich), $Zn(NO_3)_2 \cdot 6H_2O$ (99%, Fluka), $SnCl_4 \cdot 5H_2O$ (98%, Riedel-de-Haen), SeO_2 (99.8%, Aldrich) and ammonia solution NH_4OH (25%, Panreac) without previous purification. Firstly, two precursor solutions were prepared, one containing the metallic salts and the other containing selenium dioxide. The metallic solution was prepared dissolving copper nitrate (2.52 mmol), zinc nitrate (1.71 mmol) and tin chloride (1.42 mmol) in 100 mL of distilled water. The metals ratio were selected as $[Cu]/([Zn]+[Sn])=0.8$ and $[Zn]/[Sn]=1.2$ to avoid additional phase formations [33,34]. The selenium dioxide solution contained 10 mmol of SeO_2 dissolved in 50 mL of distilled water. After that, both solutions were mixed and homogenized using a magnetic stirrer. The resulting solution was put under vigorous stirring. And ammonia was added drop-by-drop until pH 6–7 in order to precipitate the selenites. Finally, the resulting powder was washed with water and ethanol and dried at room temperature.

2.2. Thin film preparation

Dispersion was prepared by mixing diethanolamine ($C_4H_{11}NO_2$ puriss. Riedel-de-Haen, abbreviated as DEA) and ethanol (C_2H_5OH Abs., Scharlau,

abbreviated as EtOH) to the obtained precipitate (mass ratio 1:1:4 → powder: DEA:EtOH). A NaI solution (0,1% in distilled water) was added to improve crystallization [35]. The mixture was stirred and sonicated for several minutes. The obtained paste was deposited on Mo-coated soda-lime glass substrates (2.5×2.5 cm² substrates) by the Doctor Blade (tape casting) method, using a glass rod as a spreader and moving along a stationary casting surface (i.e ceramic tile). An ordinary transparent tape (0.1 mm) determined the layer thickness. The film was pre-heated at 300°C on a hot plate for 2 min. The thickness of the as-deposited layers ranged between 4–4.5 μm. A thermal treatment was performed on the films in a three zone tubular furnace with Ar as a carrier gas (in static conditions). The electable S and Sn were provided as solids in suitable crucibles. The applied thermal cycle was: 20°C per minute heating speed until 550°C and 30 min of soaking time. Free cooling was used [36]. Finally, etching with water solution of NH_4S (4–22%, w/w) and KCN (2%, w/v) during 1 min (each solution) consecutively was performed to eliminate possible secondary phases ($NH_4S \rightarrow Sn(S, Se)$ and $KCN \rightarrow Cu_x(S, Se)$) [37].

The devices were fabricated by adding the subsequent layers: CdS layer (60 nm) made by chemical bath deposition (CBD), followed by i-ZnO (50 nm) and ITO (Indium-Tin Oxide, 350 nm) by DC-pulsed sputtering (model CT100 Sputtering System, Alliance Concepts). For the optoelectronic characterization 3×3 mm² cells were scribed over the absorber layer (layer deposited over 2.5×2.5 cm² Mo-coated soda-lime glass substrate) using a microdiamond scribe MR200 OEG (metallic grids or antireflective coatings were not used) [41].

2.3. Characterization techniques

Powder atomic composition was studied by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) Agilent 7500 C. Thin film composition was obtained by X-ray Fluorescence (XRF) spectroscopy (Fisherscope XVD). The crystal structure of the materials was observed by X-ray powder diffraction (XRD) with a SIEMENS D5000D diffractometer. The data were collected by step-scanning from 20 to 70° 2θ with a step size of 0.05° 2θ and 1 s counting time per step. The X-ray photoelectron spectra (XPS) of the samples were measured with a SPECS apparatus equipped with a Phoibos 100 analyzer and a 5MCD detector. The morphology of powders and films were determined by Scanning Electron Microscopy (SEM), using a Leica-Zeiss JEOL 7001F, and Transmission Electron Microscopy (TEM) applying a JEOL 2100 microscope. Both devices were equipped with a spectrometer for Energy dispersive X-ray energy spectroscopy (EDS). Phase analysis was carried out with Raman HR800-UV Horiba-Jobin Yvon spectrometer coupled with an Olympus metallographic microscope. Backscattering measurements were made using a 442 nm, 532 and 633 nm excitation wavelengths with the laser spot focused on the surface of samples. Optical absorption spectrum was recorded using VARIAN Cary 500 Scan UV–Vis–NIR spectrophotometer. The current-voltage (I-V) characteristics of the solar cells were carried out using a solar simulator (Sun 3000class AAA, Abet Technology) in standard illumination conditions: AM 1.5 and 100 mW/cm².

3. Results and discussion

The CZTSSe layers were fabricated using a modified precipitation method described previously for CIGS absorber layers [38,39]. The process is divided on three-stages: 1) precipitation of metal selenites; 2) paste preparation, deposition and pre-heating and 3) reactive (thermal) treatment for kesterite crystallization. Each synthesis step is described hereafter.

3.1. Synthesis procedure

In order to determine the precipitation conditions, several theoretical simulations were carried out by HYDRA program (software for creating chemical equilibrium diagrams). Diagrams for ionic species as

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