Solar Energy Materials & Solar Cells 160 (2017) 233–240

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

A solution approach to p-type Cu_2FeSnS_4 thin-films and pn-junction solar cells: Role of electron selective materials on their performance

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ARTICLE INFO

Keywords:
Cu_2FeSnS_4 (CFTS) thin-films
pn-junctions formed through SILAR method
Solar cell characteristics
Band-diagram from scanning tunneling spectroscopy
Junction properties and device resistances

ABSTRACT

We present formation of Cu_2FeSnS_4 (CFTS) thin-films through successive ionic layer adsorption and reaction (SILAR) method. We have considered a range of chalcogenides as *n*-type compound semiconductors, also formed through SILAR method, in conjunction with the *p*-nature of CFTS to fabricate and characterize *pn*-junction solar cells. The film-deposition method, which is a low temperature and non-vacuum one and is also suitable for obtaining films of large-areas, has maintained a balance between fabrication cost and phase purity. From scanning tunneling spectroscopy and correspondingly density of states of the semiconductors, we have estimated their band-edges to draw energy-level diagram of the devices. This has led in establishing a correlation between the band-alignment in the *pn*-junctions and energy conversion efficiency of solar cells based on the junctions. The correlation has been further supported by diode parameters of the junctions. An energy conversion efficiency of 2.9% with promising reproducibility could be achieved in CFTS|Bi_2S_3 junctions formed through this room-temperature film deposition route.

1. Introduction

In research arena of photovoltaics, achievement of high efficiency has not diluted the urge of fabricating devices with newer materials, which should be composed of earth-abundant, atoxic, and inexpensive elements. A number of materials have been investigated in this direction, among them Cu_2S, SnS, FeS_2, Bi_2S_3, and so forth can be referred right away [1–4]. Specially, the emergence of quaternary chalcogenides, $Cu_2ZnSn(S,Se)_4$ (commonly known as CZTSSe) was a noteworthy footstep in this trend [5,6]. Besides *p*-type conductivity due to cation vacancies, its optimal optical band-gap, a high absorption coefficient, and ease of synthesis [7,8] have made them a widely researched material achieving an power conversion efficiency (η) of about 12.6% [9]. Apart from pristine CZTSSe, efforts have been made to substitute zinc by cadmium yielding an efficiency of more than 9% [10]. Materials with structures, band-gaps, and absorption coefficients analogous to those of CZTSSe, such as Cu_2MSnS_4, where M=Mn, Fe, Co, or Ni, have been recently synthesized and reported [11–16]. Amongst them, Cu_2FeSnS_4 (CFTS) is considered to be a potential material for its use in a variety of light harvesting devices, such as water-purification and counter electrode in dye-sensitized solar cells (DSSCs) [16–20].

So far as the fabrication of CFTS is concerned, several vacuum and non-vacuum based methods have been developed so far [16,17,21–23]. Amongst them, solution-based deposition techniques are particularly attractive for their low-cost and easy-processing approach [19,24]. However, some of these reported methods involve the use of toxic organic solvents [14,18,20,25] and remanent insulating ligands [16,22]. Therefore, preparation of ligand-free CFTS thin films using nontoxic precursors has remained a challenge for their use in large-area photovoltaic devices. Successive ionic layer adsorption and reaction (SILAR) is a promising film-fabrication procedure that often provides an excellent balance between film-quality and cost [26–28]. The method is also appropriate to form large-area films on virtually any kind of substrates. With SILAR films of CZTS, photovoltaic devices were fabricated with *n*-type CdS formed through chemical bath deposition method; η of such devices was limited to around 2% primarily due to presence of secondary phases [28]. SILAR films of CZTS have also been used to fabricate photoelectrochemical cells [29].

Here we present a maiden report on formation of superior-quality, single-phase, and highly-crystalline CFTS thin-films through SILAR technique followed by introduction of such films in *pn*-junction solar cells. To form the heterojunctions, SILAR films of several *n*-type semiconductors have been considered, so that both the components of *pn*-junctions could be formed through SILAR method maintaining the devices to remain ligand-free. In this work, we have studied the correlation between band-alignment in the *pn*-junctions and open-circuit voltage (V_{OC}) and η of such heterojunction solar cells. The band

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http://dx.doi.org/10.1016/j.solmat.2016.10.037
Received 9 July 2016; Received in revised form 12 October 2016; Accepted 23 October 2016

gap of *n*-type semiconductors ranged from 2.4 eV (CdS) to 1.3 eV (Bi_2S_3) and finally to 1.1 eV (Ag_2S). The champion device formed through this method has yielded a power conversion efficiency of 2.9% with promising reproducibility.

2. Experimental

2.1. Formation of CFTS thin-films by SILAR method

The cationic precursors consisted of 0.1 M $SnCl_2 \cdot 2H_2O$, 0.1 M $Fe(NO_3)_3 \cdot 9H_2O$, and 0.2 M $CuSO_4 \cdot 5H_2O$ in ethanol. The compounds were added in sequence allowing sufficient time to dissolve the solutes. The transparent $SnCl_2$ solution turned golden-yellow upon addition of $Fe(NO_3)_3$ maintaining its homogeneity. Addition of copper precursor resulted greenish-yellow coloration albeit with a little amount of turbidity. The anionic precursor, on the other hand, comprised of 0.4 M $Na_2S \cdot xH_2O$ in ethanol.

During formation of CFTS thin-films, substrates were first dipped in a bath containing the cationic precursors. After allowing 30 s for their adsorption, the substrates were rinsed in ethanol followed by air-drying. They were then immersed in the anionic precursor for 45 s followed by an identical rinsing and drying protocol. This completed one cycle of SILAR film formation. Repetition of such a cycle resulted films of increased thickness, which was optimized to achieve a most favorable η. We have observed that 20 SILAR layers of *p*-type semiconductor (210 nm) had been the optimal for *pn*-junction solar cells. The thickness of *n*-type materials was optimized to around 200 nm. For metal-semiconductor Schottky junctions based on CFTS, 40 SILAR layers of CFTS (390 nm) expectedly yielded an optimum device efficiency. The thickness of the layers was measured from atomic force microscopy (AFM) images of an intentional scratch on the films.

2.2. Formation of CdS, Bi_2S_3, and Ag_2S thin-films by SILAR method

Thin-films of the *n*-type semiconductors were formed following reported routes with some modifications [26,30,31]. For CdS, equimolar (0.1 M) $Cd(NO_3)_2$ and $Na_2S \cdot xH_2O$ solutions in ethanol were used as a cationic and an anionic precursor, respectively, for adsorption in alternate. While $AgNO_3$ was the cationic precursor for Ag_2S, $BiCl_3$ was the chosen precursor for Bi_2S_3. The precursors for both these semiconductors were dissolved in methanol. Molarity of the solutions was fixed by considering *chemical formula of the compounds.*

2.3. Characterization of the materials

The materials were characterized by optical absorption and Raman spectroscopy, X-ray diffraction (XRD) patterns, field emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) along with energy dispersive X-ray analysis (EDXA), and X-ray photoelectron spectroscopy (XPS). The measurements were carried out with a Shimadzu UV-2550 Spectrophotometer, Horiba Jobin-Yvon Raman triple grating spectrometer system (model number T64000) using 514.5 nm excitation of an Argon-ion laser source (Stabilite 2017, Spectra Physics), Bruker D8 Advanced X-ray Powder Diffractometer (Cu K_α radiation, λ=1.54 Å), JEOL JSM 6700F field emission SEM, Jeol JEM-2100F TEM, and an XPS instrument (Omicron: Serial no. 0571), respectively.

In addition, the materials were characterized with a scanning tunneling microscope (STM) by using a Nanosurf Easyscan2 STM in an ambient condition to record tunneling current through ultrathin films of the materials, which were deposited on highly-doped silicon wafers (*n*-type; 3–10 mΩ cm). From tunneling current through a monolayer, we determined differential conductance (dI/dV) that has correspondence to the density of states (DOS) of materials. This enabled us to locate conduction and valence band-edges (CB and VB, respectively) of the semiconductors with respective to their Fermi energy. Since bias was applied with respect to the substrate, the tip withdrew electrons from the semiconductor at a positive voltage; peaks in the positive voltage of DOS spectrum therefore inferred location of VB of the semiconductors. Similarly, peaks at negative voltages, at which electrons could be injected to the semiconductors, provided the location of their CB edges. The morphology of the films was imaged with a Nanosurf Easyscan2 Atomic Force Microscope (AFM) in a non-contact mode.

2.4. Fabrication of devices

The devices were formed on patterned indium tin oxide (ITO) glass substrates having a sheet resistance of 15 Ω/square. The substrates were cleaned and treated with ozone for better interfacial contact with its immediate layer. Since we aimed to form a direct device-structure, a hole-transport layer (HTL) was first formed on the substrates. To do so, a precursor solution of Cu@NiO (5 at%), which was formed through a well-documented sol-gel method, was spun on the substrates at 3000 rpm for 30 s followed by annealing at 425 °C in air for 15 min. Since each step produced a ~20 nm thick film, we repeated the process to achieve a ~40 nm film of the HTL. The active layers of *pn*-junctions, namely *p*-type CFTS and *n*-type chalcogenides (CdS, Bi_2S_3 or Ag_2S) were formed in sequence following the as-stated SILAR technique. The films were annealed after formation of each layer at 150 °C for 15 min in nitrogen environment to reduce the possibility of oxidation. Here, we intentionally refrained from carrying out sulfurization or selenization of the thin-films so that the solar cells could be formed without any high-temperature annealing. As an electron-transport layer (ETL), thin-films of ZnO nanoparticles were formed by spin coating from a 30 mg/mL solution in ethanol at 3000 rpm for 30 s. The multilayered films were again annealed at 120 °C for 15 min in nitrogen environment. Finally, thermal evaporation of aluminum in vacuum led to formation of a 100 nm top electrode orthogonal to the ITOs. This completed fabrication of 4–5 cells having an effective area of 10 mm^2 each (Fig. S1 in the Supplementary section).

2.5. Characterization of the devices

Current-voltage (*I-V*) characteristics of the devices under a dark and a range of illumination conditions were recorded with a Keithley 2636 Electrometer using LabTracer software. Devices were kept in the glovebox in order to avoid oxidation of the top aluminum electrode and were connected to the electrometer via 3 axis micro-positioner having pressure-loaded spring probe contacts. A 300 W Solar Simulator (Newport-Stratfort model 76500) attached with an AM1.5 filter placed outside the glovebox acted as a source for illumination. Intensity of the simulated solar light on the device was 100 mW/cm^2. While recording *I-V* characteristics under an illumination condition, regions outside the cell-area were covered to avoid any contribution from neighboring areas or cells. Intensity of the simulated solar light was varied between 10 and 100 mW/cm^2 that was tuned with neutral density filters. To record external quantum efficiency spectrum of solar cells, a 1/8 m monochromator (Oriel Cornerstone 130) was used to disperse the simulated solar illumination; the corresponding photocurrent was measured with a Hewlett-Packard 34401A digital multimeter.

3. Results and discussion

3.1. Characterization of CFTS thin-films

A XRD pattern of as-formed CFTS thin-films is shown in Fig. 1a. All the intense peaks were in excellent agreement with stannite phase of the material (JCPDS Card Number 44-1476). The diffraction peaks have a narrow full-width at half-maxima (FWHM) indicating a high-degree of crystallinity of the material in thin-films. The lower-limit of crystallite size, as calculated from Scherrer equation, turned out to be