Solar Energy 158 (2017) 89–99

Contents lists available at ScienceDirect

Solar Energy

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

Fabrication of Cu_2CoSnS_4 thin films by a facile spray pyrolysis for photovoltaic application

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ARTICLE INFO

Keywords:
CCTS thin films
Spray pyrolysis
Stannite structure
Optical properties
Contact angle
Photoelctrochemical cell

ABSTRACT

The role of substrate temperature on the structural, morphological, optical, and photovoltaic properties of Cu_2CoSnS_4 (CCTS) thin films based on earth abundant and non toxic elements, has been presented. Thin films of CCTS have been deposited by spray pyrolysis technique. X-ray diffraction study revealed that the films are polycrystalline in nature with stannite structure. Raman analysis confirmed the phase purity of CCTS films deposited at substrate temperature of 350 °C. The XPS spectra indicates oxidation states of Cu, Co, Sn, and S to be Cu^{+}, Co^{2+}, Sn^{4+}, and S^{2-} in CCTS films. FE-SEM images showed drastic variation in the morphology of the films with respect to increase in substrate temperature. EDAX spectra of the films deposited at different substrate temperatures revealed the presence of different constituent elements such as, Cu, Co, Sn and S in CCTS thin films. The energy band gap values for the films were found to be decreasing from 1.79 eV to 1.42 eV with respect to increase in substrate temperature. The static contact angle measurement of the films with Sodium sulphate electrolyte depicts the hydrophilic nature of the films. The photoelectrochemical solar cell has been constructed using Sodium sulphate as electrolyte, platinum as counter electrode, while CCTS thin films were used as working electrodes. The power conversion efficiency of 1.78 % and open circuit voltage of 350 mV was observed for the CCTS thin films deposited at substrate temperature of 350 °C.

1. Introduction

Electricity generation by photovoltaics can be adopted to reduce increasing strain on fossil fuels, as solar energy which is the most abundant and renewable source of energy on earth (Edoff, 2012). For the commercial solar cells based on silicon, much thick layer of absorber material greater than 100 µm is essential to absorb considerable amount of incident solar radiation. Additionally perfect single crystal substrates are required to build a highest efficiency solar module which contributes to increasing cost of silicon solar cells (Mitzi et al., 2011). For the thin film solar cells (TFSC) derived from the materials like CdTe, $CuInSe_2$ (CIS) and $CuInGaSe_2$ (CIGS) there are issues in supply of In and Te that may limit the production capacity of the photovoltaic devices. To surmount the issues of toxicity and production cost using naturally abundant elements, new materials have to be explored and must be employed for escalating efficiencies of TFSC (Wang, 2011). Cu_2CoSnS_4 (CCTS) is a p-type compound semiconducting absorber material, with band gap in the range of 1.46 eV–1.61 eV. Owing to the optimal band gap value of CCTS, there is effective enhancement in the absorption at absorber layer, which significantly reduces the material need over the other indirect band gap alternative materials like crystalline silicon (Xie et al., 2017). The availability of copper, cobalt, tin, and sulfur in earth's crust is found to be 50 ppm, 20 ppm, 2.2 ppm, and 260 ppm respectively. To decline the pressure on current photovoltaic (PV) technology much attention should be provided on development of PV technology rooted in abundant and nontoxic elements like CCTS (Hossain, 2012). The low-cost and high-efficiency alternatives to the conventional absorbing materials in photovoltaics like CdTe, $CuInSe_2$ (CIS) and $CuInGaSe_2$ (CIGS), are copper-based ternary I–IV–VI and quaternary I–II–IV–VI nanocrystals (NCs) with II (Mn, Fe, Co, Ni, Zn, Cd, Hg) and IV (Si, Ge, Sn) (Liu et al., 2013). There are variety of techniques by which the compound semiconductor CCTS has been synthesised such as, hydrothermal (An et al., 2003), solvothermal (Chane-Ching et al., 2011; Cui et al., 2012; Mokurala et al., 2016), sol-gel (Murali et al., 2014), hot injection (Gupta et al., 2015), solid state reaction (López-Vergara et al., 2015), electrospinning (Gonce et al., 2016; Ozel, 2016; Ozel et al., 2015), high temperature route (Benchikri et al., 2012; Zaberca et al., 2011), melt and anneal process (Gulay et al., 2004;

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http://dx.doi.org/10.1016/j.solener.2017.09.036
Received 6 June 2017; Received in revised form 6 September 2017; Accepted 16 September 2017
0038-092X/

Quintero et al., 2014). The majority of the CCTS research has been dedicated to the synthesis of nanocrystals. To facilitate the possibility of practical application in photovoltaic devices, the CCTS thin films need to be thoroughly studied. In order to reduce high manufacturing cost of large scale solar cell production it is essential to adopt single step process that is more suitable and economic. Among the diverse methods accessible for deposition of thin films, the spray pyrolysis technique is widely used and has many advantages such as non-vacuum, easy handling and large deposition area (Desai et al., 2015).

To carry out the deposition of thin films by spray pyrolysis, electronic control system has been developed to maintain the temperature of heater. The system is designed around open source Arduino microcontroller platform along with 0 °C to 1000 °C range K-type thermocouple and MAX6675, to sense the temperature of heater plate. Closed loop arrangement is used to develop electronic control system. The working temperature range is selected in the range of (± 2) °C with respect to threshold set point entered by user. Control system used here provides a simplified user interface for desired temperature setting, with the help of single push button switch and potentiometer. A solid state relay (230 V/25 A) is used to make ON/OFF arrangement of heater to keep the temperature in the desired range. The process flow such as, display of current temperature and attainment of working temperature value from user is displayed on 16 × 2 LCD. In addition, control system handles automatic movement of nozzle through a slider crank mechanism, aided by dc geared motor. The dc motor used for this purpose has a rotational speed of 10 rpm, and requires 12 V of operating voltage. It has shaft diameter of 6 mm and offers a torque of 12 kg-cm.

This paper represents the effect of substrate temperature on structural, morphological optical and photovoltaic properties of CCTS thin films prepared by spray pyrolysis technique.

2. Experimental details

Fig. 1 shows the schematic of the spray pyrolysis unit used for deposition of CCTS thin films. The reaction chamber of spray pyrolysis unit has dimensions of 90 cm (length) × 60 cm (breadth) × 90 cm (height). The different byproducts evolved during the pyrolysis were removed by exhaust fan fitted to reaction chamber. The atomization of the precursor solution was achieved by filtered compressed air. The pressure of the compressed air was kept at ≈1 bar. To accomplish the regular deposition of the thin films mechanized to and fro movement, with frequency of 0.16 Hz has been employed to spray nozzle.

The CCTS thin films, were deposited with the precursors $CuCl_2{\cdot}2H_2O$ (Cupric Chloride) for copper, $CoCl_2{\cdot}6H_2O$ (Cobalt Chloride Hexahydrate) for cobalt, $SnCl_4{\cdot}5H_2O$ (Stannic Chloride) for tin and CH_4N_2S (thiourea) for sulfur. The precursor solution for deposition of CCTS films consist of 0.05 M $CuCl_2{\cdot}2H_2O$, 0.025 M $CoCl_2{\cdot}6H_2O$, 0.025 M $SnCl_4{\cdot}5H_2O$, while excess amount of thiourea was chosen than the stoichiometry to avoid the loss of sulfur at elevated temperature (Ghosh et al., 2016a). All the solutions were prepared in methanol. When all the cationic solutions were mixed together the color of the solution was brown with pH of the resulting solution ≈1. Thiourea was added drop wise to this cationic solution under vigorous stirring. When complete thiourea was added to this cationic solution, the pH of the resulting solution turned to ≈ 3. The final color of precursor solution was observed to be dark blue.

With a flow rate of 5 mL/min, 80 mL of the precursor solution was sprayed onto SLG (soda lime glass) and FTO (Fluorine doped Tin Oxide) substrates; which were preheated using temperature control arrangement. The SLG and FTO substrates were kept on circular stainless steel plate with diameter of 20 cm and thickness of 0.5 cm. Deposition of the thin films was carried out in the temperature range of 250 °C–400 °C with an interval of 50 °C.

Surface profiler (Ambios, XP-I stylus profiler, USA) was used to carry out the thickness measurement of the films. The structural properties of spray deposited CCTS films were studied by using X-ray diffractometer (XRD) operated at 40 kV, 30 mA with Cu K_α radiation (λ = 1.54 Å). The Raman analysis was carried out with the help of Renishaw inVia micro-Raman spectrometer at excitation wavelength of 633 nm of He-Ne laser as an excitation source. The XPS analysis was done using X-ray photoelectron spectrometer (Kratos Analytical, ESCA 3400) with monochromatic Al K_α 600 W X-ray source. The surface morphology of the films was studied with a MIRA 3 FE-SEM microscope (TESCAN) attached with EDX detector (Oxford Instruments, UK). UV–Visible spectrophotometer (UV 1800, Shimadzu, Japan) was used to record UV–Visible absorbance spectra of the films.

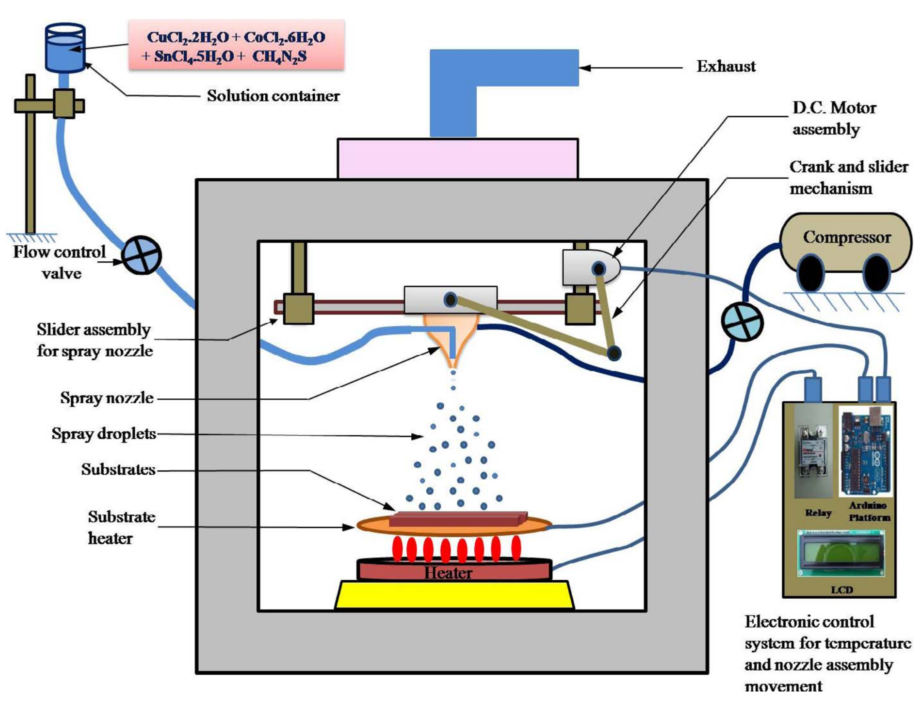

Fig. 1. The schematic representation of spray pyrolysis unit used for deposition of CCTS thin films.