Journal of Analytical and Applied Pyrolysis 122 (2016) 230–240

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Vanadium doping induces surface morphological changes of $CuInS_2$ thin films deposited by chemical spray pyrolysis

T. Logu [a], K. Sankarasubramanian [a], P. Soundarrajan [a], J. Archana [b], Y. Hayakawa [b], K. Sethuraman [a,*]

[a] School of Physics, Madurai Kamaraj University, Madurai – 625 021, Tamil Nadu, India
[b] Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka 432-8011, Japan

ARTICLE INFO

Article history:
Received 19 September 2015
Received in revised form
20 September 2016
Accepted 23 September 2016
Available online 28 September 2016

Keywords:
CIS films
Optical properties
Raman spectroscopy
Electrical properties

ABSTRACT

Pristine and vanadium (V) doped $CuInS_2$ (CIS) thin films were grown on glass substrate using home-built chemical spray pyrolysis unit. The structural, morphological, optical and electrical properties of pristine and V doped CIS thin films have been systematically inspected. The scanning electron and atomic force microscopic (SEM and AFM) images show the well-interconnected CIS nanoparticles changed to nanorods like morphology with respect to V doping level and also the number density of the nanorods increases with doping level. Furthermore, the formation of CIS nanoparticles and V doped CIS nanorods are authentically confirmed by the transmission electron microscopic (TEM) images. Both pristine and V doped CIS thin films exhibit the body centered tetragonal crystal structure along with polycrystalline nature which is characterized using X-ray diffraction (XRD) and selected area electron diffraction (SAED) patterns. The presence of dopant and host elements is confirmed by X-ray photoelectron and energy dispersive X-ray spectroscopic (XPS and EDX) analyses. The decreases of orbital energy gap values are observed using UV–Vis absorption spectra according to V doping level into the CIS lattice sites. A continuous suppression of defect related Cu-Au orderings are observed via Raman spectra as a function of V doping which also indicate the V doping significantly involved during deposition and improve the structural quality of the chalcopyrite CIS film. The electrical properties of CIS films transform enormously, switching from hole dominated ($0.3782\,S\,cm^{-1}$) p-type to electron dominated ($27.16\,S\,cm^{-1}$) n-type from 4 wt.% of V doping. It anticipates that this kind of self-assembled 1D CIS nanostructure will give huge interest to tune their physicochemical properties.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

$CuInS_2$ (CIS) is one of the I–III–VI_2 semiconductors and consider being a promising absorber layer material in solar cells, which has special attention among researchers from last decade due to its excellent physical properties such as optical and electrical and non-toxic characteristic [1]. Hitherto, the efficiency of CIS absorption layer based solar cells has been achieved to be 12.5% in the laboratory scale [2]. But, it is quite lower than the efficiency (∼28%) anticipated in theoretically [3]. This large difference from the theoretical value is due to the presence of atomic level defects in CIS films. Thus, if defect-related problems are solved gradually by depositing good crystalline film via controlling synthetic strategy and/or adding impurity, the higher conversion efficiency could be achieved in *cis*-based solar cells.

The CIS thin films have been deposited by several techniques such as solution growth [4], chemical vapor deposition [5], sputtering [6] and chemical spray pyrolysis [7]. To enhance the optical and electrical properties, several impurity ions doped with CIS films have been successfully reported. W.J. Tsai et al. examined the effect of Na on CIS thin films that significantly improves the structural and optical properties [8]. The structural and optical properties of Na doped CIS thin films deposited using double source thermal evaporation were also investigated by Zribi et al. [9]. The influence of aluminum doping on CIS thin films has been studied by N.K. Allouche et al. [10]. Akaki et al. reported the structural, electrical and optical properties of Bi doped CIS thin films grown by vacuum evaporation method [11]. Among them, some of the dopants are found to control the conduction type and obtaining a low resistivity in CIS film [8–11]. These reports clearly reveal that the doped CIS is essential material in the field of photovoltaic applications. In

* Corresponding author.
E-mail address: sethuraman_33@yahoo.com (K. Sethuraman).

http://dx.doi.org/10.1016/j.jaap.2016.09.019
0165-2370/© 2016 Elsevier B.V. All rights reserved.

particular, the conduction type controlled CIS film is used for engineering the heterojunction solar cells. Hence, the chemical spray pyrolysis is an attractive method for the deposition of large scale production due to its simplicity and cost effectiveness and also a very powerful method to dope any element during deposition. It has been used to deposit the photovoltaic structures, including CIS solar cells and achieved average efficiencies around 5–6% [12–14]. Previously much work have been done on CIS material using spray pyrolysis where also investigated the effects of deposition parameters like substrate temperature [15], volume ratio [16]. Very few works have been reported on the doped CIS thin films.

It obviously observed that the morphological structure changes of CIS films via doping process by chemical spray pyrolysis is not clearly discussed in the previously reported articles. Hence, our research team for the first time deposit pristine and V doped CIS thin films using chemical spray pyrolysis technique. After that we desperately involved to explain the effects of V doping on spray deposited CIS films using structural, morphological, optical and electrical characterizations. To the best of our knowledge, the randomly aligned self-assembled one-dimensional (1D) V doped CIS nanorods structure thin films were fabricated at the first time by chemical spray pyrolysis method.

2. Experimental details

Pristine and V doped CIS thin films were deposited on glass substrate ($2.5 \times 2.5 \times 0.15\,cm^3$) using chemical spray pyrolysis unit. Initially, 0.1 M of copper (II) chloride, indium (III) chloride and thiourea were separately taken and dissolved in double distilled water. Then they were mixed with appropriate portions in order to have copper to indium molar ratio (Cu/In = 1) and (Cu + In)/S fixed to 1 in the solution. The copper (II) chloride and thiourea are mixed and then indium (III) chloride solution was added. It is well known that the accuracy of synthetic parameters mainly depends on the error bar of the instrument. Hence, our research team carefully constructs the spray pyrolysis unit as shown in Fig. 1. The noted points in schematic diagram are (1) air compressor (2) precursor solution (3) nozzle (4) droplet (5) substrate (6) hot plate (7) thermocouple (8) PID controller and (9) exhaust system respectively. Prior to deposition, the glass substrates were ultrasonically cleaned in acetone, ethanol and double distilled water separately. The substrate temperature was fixed at 350 °C with the help of PID temperature controller. In each deposition, the nozzle to substrate distance was maintained at 24 cm, and then the 45 mL of precursor solution was sprayed at a rate of 3.5 mL/min on preheated glass substrate. At substrate temperature of 350 °C, the solvent (double distilled water) evaporates before the droplet reaches the substrate. Then the CIS precipitate melts and vaporizes in air without decomposition. Finally, the vapor diffuses on the glass substrate to undergo thermal decomposition process [17]. Different weight percentage (2, 4, 6 and 8 wt%) of vanadium (III) chloride was added in the above precursor solution for V doping.

The pristine and V doped CIS films thicknesses were measured using Ambios, XP2 surface profiler. The crystalline phases of the prepared samples were examined by Brucker D8 Advanced X-ray diffractometer (XRD) using a Cu K_α radiation in the 2θ range of 20–70°. Further, the particle size, shape and crystalline nature of prepared samples were confirmed by TECNAI T20 high resolution transmission electron microscopy which operated at 200 kV accelerating voltage. The surface morphology of the thin films was observed using a scanning electron microscopy (SEM, Helios-Nano 600 me, FEI Quanta). The presence of host and dopant elements were analyzed using energy dispersive X-ray analysis (EDX) followed by SEM imaging. Furthermore, the 8 wt% of V doped CIS thin film exampled to X-ray photoelectron spectroscopy (XPS). The 2D and 3D topography and root mean squared (RMS) surface roughness of the prepared films were elucidated by atomic force microscopy (AFM) (Non-contact mode, A100 SGS, APE Research). The structural phases of pristine and V doped CIS thin films were further analyzed using a 632.8 nm He–Ne laser line from a LabRam HR800 micro-Raman instrument, and its backscattering mode recorded in the wave number range of 100–400 cm^{-1}. The optical absorption spectra of prepared films were then measured using UV–VIS spectrophotometer (SHIMADZU UV-1800). Continuously, the photoluminescence spectra were recorded for the prepared thin films using SHIMADZU-5301 spectrofluorometer. The electrical properties of the films were studied using the Hall measurement setup in Vander Pauw configuration (Ecopia HMS-3000).

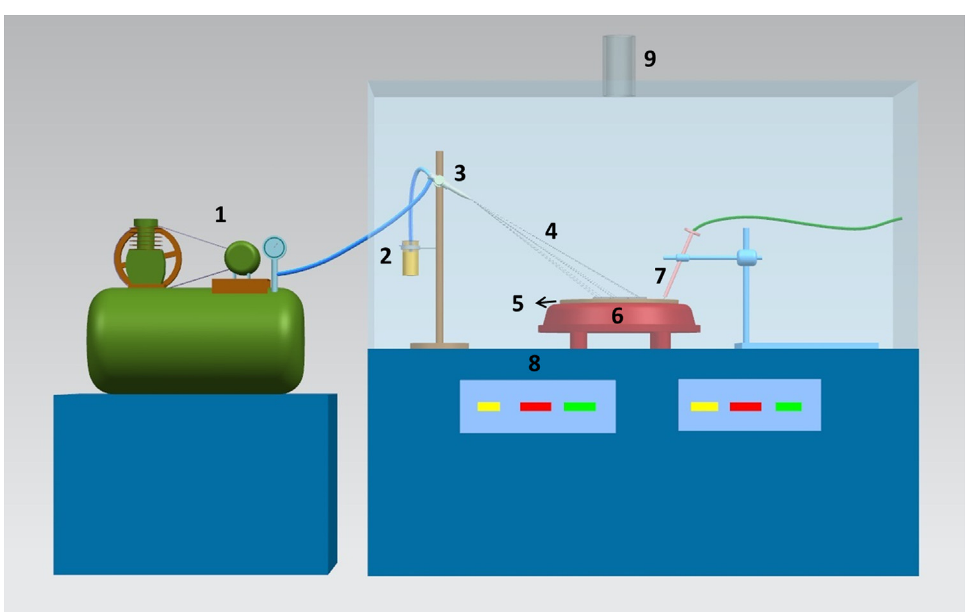

Fig. 1. Schematic diagram of chemical spray pyrolysis setup.

Download English Version:

https://daneshyari.com/en/article/5134773

Download Persian Version:

https://daneshyari.com/article/5134773

Daneshyari.com