Cost Effective Synthesis and Fabrication of Phase-Pure Kesterite Cu$_2$xZn$_{1.3}$SnS$_4$ P-type Absorber Layer Thin Films by Solvent Based Process Technique for Photovoltaic Solar Energy Applications

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Abstract—Solar has become one of the fastest growing renewable energy sources. With the push towards sustainability it is an excellent solution to resolve the issue of our diminishing finite resources. Alternative photovoltaic systems are of much importance to utilize solar energy efficiently. The Cu-chalcopyrite compounds CuInS$_2$ and CuInSe$_2$ and their alloys provide absorber material of high absorption coefficients of the order of 10$^5$ cm$^{-1}$. Cu$_2$ZnSnS$_4$ (CZTS) is more promising material for photovoltaic applications as Zn and Sn are abundant materials of earth’s crust. Further, the preparation of CZTS-ink facilitates the production of flexible solar cells. The device can be designed with Al doped ZnO as the front contact, n-type window layer (e.g. intrinsic ZnO); an n-type thin film buffer layer (e.g. CdS) and a p-type CZTS absorber layer with Molybdenum (Mo) substrate as back contact. In this study, CZTS films were synthesized by a non-vacuum solvent based process technique from a molecular-ink using a non toxic eco-friendly solvent dimethyl sulfoxide (DMSO). The deposited CZTS films were optimized and characterized by XRD, UV-visible spectroscopy and SEM.

Keywords—Chalcopyrite, CZTS Molecular-Ink, Kesterite, absorber layer, Photovoltaic, Solar energy.

I. INTRODUCTION

Photovoltaic systems have been gaining in importance in order to utilize solar energy efficiently. The copper chalcopyrite compounds, CuInS$_2$ and CuInSe$_2$ and their alloys can be used as absorber materials with high absorption coefficients of the order of 10$^5$ cm$^{-1}$. CZTS is a promising thin film p-type absorber material for solar cell fabrication, owing to its earth’s abundance and environment compatible nature. CZTS results by replacing indium and gallium by less expensive, earth abundant zinc and tin, from CIGS (Copper Indium Gallium Selenide), to make it a less expensive p-type absorber material for solar cell fabrication [1]. CZTS is an I$_2$-II-IV-VI$_4$ quaternary compound. There are various different types of methods developed for fabricating kesterite thin films. Some of the versatile methods are vacuum based deposition technique, chemical vapor deposition, electrodeposition technique, and chemical route sol-gel technique. Qijie Guo et.al, 2009, [2] reported the first synthesis of Cu$_2$ZnSnS$_3$ nanocrystals using hot injection method and demonstrated its use for the fabrication of solar cells, but the efficiency was less than 1%. With slight changes in the amount of precursors (at non-stoichiometric conditions of CZTS nanocrystals) Qijie Guo et.al, [3] achieved 7.2% efficiency. CZTS material based solar cells have reached a power conversion efficiency upto 9.2% till date [4]. Sunil et.al, [5] predicted that basic defect physics of the material and its influence on phonon spectrum to transport properties may reveal the mechanism behind surge in efficiency under non-stoichiometric conditions. Solvent based
process technique can be sub-divided into two categories, (i) based on the formation of CZTS kesterite crystalline structure before the deposition of the nanocrystalline ink on the soda lime glass substrate, (ii) based on the surface precursor reactions upon annealing the CZTS-ink deposited substrate. The solvent based process method of synthesizing CZTS-ink involves the formation of p-type absorber layer thin films with reduced secondary phases, directly from the as synthesized molecular-ink which are non-toxic true solutions whereas are not slurries as in the case of hydrazine based hot-injection technique [6]–[7].

II. EXPERIMENTAL DETAILS

The CZTS films were synthesized and deposited from a molecular-ink using solvent based process method which uses an eco-friendly non-toxic solvent, dimethyl sulfoxide (DMSO) to fabricate efficient polycrystalline solar cells. The true solution was synthesized by dissolving the precursors of copper, zinc and tin one by one in DMSO solvent for optimised time based on its solubility. At the last, the final chemical of sulphur precursor was added to the solution, resulting in the formation of CZTS -ink. The precursor solution was synthesized by the simultaneous addition of metal precursors into the DMSO solvent, kept under stirring at constant rpm. The metal precursors were added in a sequential order based on the reactivity series, Cu < Zn < Sn. Initially, 8 ml of DMSO was added to a 25ml beaker having copper precursor, 6mM of copper acetate monohydrate at ambient temperature. This results in the formation of a deep blue colored solution because of the limited solubility of copper acetate monohydrate in DMSO solvent. This was followed by the addition of zinc precursor, 5.5mM of Zinc Nitrate, into the deep blue colored solution which was kept under stirring at a constant rpm at ambient temperature. Gradually the deep blue colour solution changed to transparent light green colour solution after 20 hours of constant stirring due to the reduction of Cu$^{2+}$ to Cu$^{+}$ followed by the stabilization of Nitrate ions and DMSO ions. This was followed by the addition of tin precursor, 5.6mM of Tin Chloride Monohydrate, into the transparent light green solution. After a constant stirring of 6 hours the transparent green colour of the metal precursor solution changed to pale greenish yellow. At last, the final chemical of sulphur precursor, i.e., 14.3mM of thio urea was added. Finally, a clear colorless solution was obtained due to the following two major reasons: 1. The sulphur precursor getting completely dissolved. 2. Due to the presence of small amount of Cu$^{2+}$ cations in the final solution. The final solution was diluted to 40% with the non-toxic environment friendly solvent DMSO resulting to the formation of non-stoichiometric Cu$_2$Zn$_{1.3}$SnS$_4$ dispersed molecular-ink. The synthesized CZTS molecular-ink was characterized to confirm its kesterite structure. The CZTS thin films were deposited by spin-coating the molecular-ink on to a soda-lime glass substrate to form CZTS p-type absorber layer film. Further, the CZTS films that were fabricated by spin coating technique was annealed at 500°C with elemental sulphur vapor (sulphurization) inorder to enhance and promote crystallinity of the thin film by partial replacement of sulphur atoms.

III. RESULTS AND DISCUSSION

In Fig.1, the X-ray diffractogram of annealed CZTS film shows the formation of pure kesterite phase, which is commonly observed for realizing efficient CZTS solar cells. Peak positions (112), (220) and (312) are indexed in the diffraction pattern which is well in agreement with the literature [5]. The lattice parameters for the CZTS nanocrystals are a = 5.427 Å, b = 5.427 Å and c = 10.848 Å [6].
From the Tauc plot of CZTS thin film in Fig. 2, it is inferred that the energy bandgap ($E_g$) of the annealed kesterite CZTS thin films is 1.4 eV.

The SEM images show that the film is very uniform with thickness ~1 µm. The surface morphology in the following Fig. 3 (a) and (b) shows the densed and crack-free films. Films prepared under Cu poor Zn rich conditions adhere well to the glass substrate.
Raman studies on Cu$_{2-x}$Zn$_x$SnS$_4$ ($x=0, 0.3, 0.5$ and $0.7$) thin films were done by changing the incident laser beam intensity. From Fig. 4, it is observed that both copper stoichiometry and incident laser beam intensity induce a disorder in CZTS. In the case of CZTS, it is reported that defect density influences phonon density of states which in turn affects carrier concentration. Therefore, it becomes important to correlate basic defect physics of materials and its influence on phonon spectrum to transport properties; which may reveal the mechanism behind surge in efficiency under non-stoichiometric conditions [5].

After optimizing the p-type (CZTS) and n-type (CdS) layers, a p-n junction have been created in order to analyze the diode characteristics. Fig. 5 shows the I-V characteristics (dark) of CZTS/CdS p-n junction.

The CZTS solar cell preparation involved the deposition of Mo, p-CZTS, n-CdS, i-ZnO and Al:ZnO layers in a sequential manner on a soda lime glass substrate in the form of a stack, as shown in Fig. 6.

The CZTS solar cell is then tested using a solar simulator (incident power 1000 W/m$^2$) for I-V characteristics and quantum efficiency studies. Fig. 7 shows the device characteristics of the fabricated kesterite phase CZTS solar cell. For the initial device a quantum efficiency of $\sim 0.39\%$ was achieved. Currently, the focus of work is to modify the processing conditions in order to get good interfaces between the materials, which will in turn enhance better efficiency of the solar cell.
Fig. 7 CZTS Solar Cell: Device Characteristics

IV. CONCLUSIONS

The CZTS films prepared by solvent based process technique from its molecular-ink using a non-toxic and ambient friendly solvent dimethyl sulfoxide (DMSO) were very uniform. They adhere to the soda lime glass substrate and shows phase-pure Kesterite CZTS with the bandgap 1.4 eV. CZTS solar cells show better efficiency in copper poor and zinc rich non-stoichiometric conditions. The solvent based process method of fabricating Kesterite CZTS thin films comparatively reduces the formation of secondary phases which are responsible to reduce the performance of the solar cell. In the case of CZTS, it is reported that defect density influences phonon density of states which in turn affects carrier concentration. Therefore, it becomes important to correlate basic defect physics of materials and its influence on phonon spectrum to transport properties; which may reveal the mechanism behind surge in efficiency under non-stoichiometric conditions [5]–[7].

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