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A novel approach for the synthesis of tin antimony sulphide thin films for photovoltaic application

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Abstract

Alternative semiconductor materials to copper indium gallium selenide (CIGS), copper zinc tin sulphide (CZTS), cadmium telluride (CdTe) is driven by the need to use less toxic and earth-abundant materials as an absorber layer in thin film solar cells. The ternary compounds based on Sn–Sb–S (TAS) compositions are deemed to be a possible replacement of existing semiconductor materials due to their low processing cost and nontoxic elemental composition. In this study thin films of tin antimony sulphide (TAS) are deposited on glass substrate from tin sulphide and antimony sulphide binary precursors, without substrate heating, combinatorially in thermal vacuum chamber. The average thickness of the library obtained was 1.2 μm as measured by quartz crystal monitor. The X-ray diffraction analyses measured by D-8 Discover diffractometer shows that the as deposited films were amorphous while the annealed films are poly crystalline. The maximum reflection was observed for the lattice plane (1 1 1) for $SnSb_2S_4$ and $Sn_2Sb_2S_5$. The optical properties of the thin films were measured by ellipsometry while electrical properties were measured by photoconductivity spectrometer and four-probe technique. The band gap was varied with variation in elemental composition as well as annealing temperature between 1.6 and 2.7 eV. It was observed that TAS exhibit bipolar conductivity at different annealing temperature.

Keywords: Tin antimony sulphide; Combinatorial deposition; Photovoltaics; Thin films; Absorbance; Resistivity

1. Introduction

The trends of current research in photovoltaics include non-toxic and earth abundant materials in thin films, dye sensitized solar cells and nanostructured materials. In thin film photovoltaics, cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) are the leading technologies in photovoltaics. These both materials contain toxic and rare materials (Sinsermsuksakul et al., 2012; Emrani et al., 2013; Dhakal et al., 2014). Sulphides are less toxic than selenides, though efficiencies of sulfo-selenide devices are up to 10.1% compared to that of sulphide devices which are only 6.8% efficient. Therefore the low toxicity and abundance of sulfosalt materials are preferred as absorber layer in solar cells (Chalapathy et al., 2011; Drissi et al., 2013; Gurav et al., 2013).

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The alternative semiconductor material tin antimony sulphide (TAS) is however not only earth abundant but also non-toxic thus could replace CdTe and CZTS. The reported optimized bang gap for TAS is ~2 eV for as deposited and ~1.4 eV for annealed films (Inamdar et al., 2013). In addition TAS has an absorption coefficient of $10^5\,cm^{-1}$ making it a promising candidate for thin film solar cells (Ali et al., 2014). The variation in band gap and other optical and electrical properties depend on elemental composition as well as growth conditions (Lehner et al., 2013; Malerba et al., 2014; Platzer-Björkman et al., 2012; Salomé et al., 2012; Shin et al., 2012). For example, TAS with Sb-poor composition is a P-type semiconductor, but as the Sb content in the composition is increased, TAS turns into N-type semiconductor.

A two stage process involving sputtering of metallic targets followed by sulphurization and thermal evaporation of SnS and Sb_2S_3 powders is a frequently used method for the deposition of TAS thin films. However, several other techniques such as spray pyrolysis, electro-deposition, pulsed laser and sol–gel deposition can also be used for the deposition. The sputtered metallic film is sulphurized by evaporating elemental sulphur in vacuum thermal coater and heating in inert atmosphere. The heating of metallic films in continuous flow of H_2S gas inside the tube furnace at high temperature is also an alternative way for the sulphurization of the libraries (Shinde et al., 2013; Fernandes et al., 2013; Ali et al., 2013; Potyrailo and Mirsky, 2009; Eason, 2007).

Our group has explored several properties of TAS using conventional methods of deposition (Ali et al., 2014a,b; Ali et al., 2013). However, it is possible to explore the properties of nearly all the elemental compositions of TAS using the novel technique of combinatorial deposition. Combinatorial deposition like multivariate chemometric approach for dye-sensitized solar cells (DSSCs) and a simulated work based on parametric runs is a rapid and convenient tool for discovering multi compositional materials in the best elemental composition from a large landscape (Bella et al., 2014; Ghiaus and Jabbour, 2012). The combinatorial approach to materials is best employed in the form of thin film combinatorial libraries. The development of combinatorial method was initially experimented for drug discovery, which was later on extended to catalysis and the discovery of new materials. The combinatorial approach referred to as "combinatorial materials science" was expanded to the discovery and design of transparent conducting materials (TCO), luminescent and shape memory alloys, ferromagnetic and piezoelectric materials, and optoelectronic devices as well. Hundreds of different compositions can be synthesized and integrated on as small as 1 cm^2 substrate for the desired elemental composition. This approach is feasible in concept for discovery of new materials with improved physical properties (Zhang et al., 2013, 2004). In this study we have utilized combinatorial approach towards the TAS thin film growth via thermal evaporation technique for photovoltaic research.

2. Experimental

Different compositions of TAS thin films were prepared on clean glass substrate by thermal vacuum evaporation using a combinatorial approach and two evaporation sources. Sb_2S_3 was purchased from Kurt J. Lesker, UK with 99.99% purity and SnS was synthesized from tin and sulphur powder by the following ratio (Massalski and Okamoto, 1990).

$Sn = 0.7873$ g

$S = 0.2127$ g

Both of the powders were mixed, ground together in a pestle and mortar, and annealed in a quartz ampoule under argon atmosphere for 24 h at 600 °C. After annealing, the powder was ground together again and hydraulically pressed to make separate pallets of SnS and Sb_2S_3 for thermal evaporation. Thin films of TAS were deposited by combinatorial technique from SnS and Sb_2S_3 pallets as shown in Fig. 1. These materials were evaporated from Al_2O_3 crucibles in vacuum chamber for combinatorial thin films on glass substrates. The pressure of the chamber was kept at about 2×10^{-4} mbar. The deposited combinatorial thin films were annealed at 85 °C, 105 °C, 150 °C, 275 °C and 325 °C in sealed glass ampoules containing argon gas.

Energy dispersive X-ray spectroscopy (EDX) "probe current 5.0 nA, beam current 200 μA" was used for elemental composition of the films. D-8 Discover diffractometer with Cu K_α radiation (wavelength, $\lambda = 1.54$ Å) was used for the structural analysis of the films. Variable angle ellipsometry (VASE) (J.A. Woollam M2000 ellipsometer) was used for the measurement of optical properties of the films over a spectral range of 300–1800 nm. This was used to determine the optical band gap and transmittance of the films, with ellipsometry data supplemented by transmission measurements was taken by the ellipsometer.

For the electrical properties of the films, molybdenum contacts were deposited 1 mm apart by dc-magnetron sputtering. Photoconductivity was measured using chopped light of variable wavelength from 350 nm to 1100 nm and a Si reference photodiode, with data collected on a PC

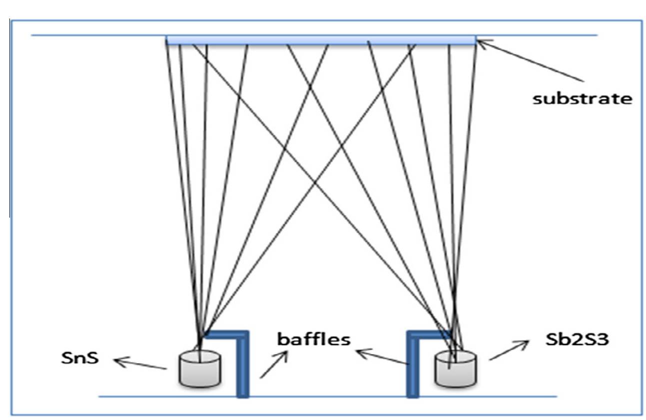

Fig. 1. Schematic for combinatorial TAS evaporator.