

Effect of sulfurization on the properties of $\text{Cu}_2\text{ZnSnS}_4$ thin films deposited using chemical spray pyrolysis over ITO substrates



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ABSTRACT

$\text{Cu}_2\text{ZnSnS}_4$ thin films with different tin concentration are deposited over ITO coated glass substrates using chemical spray pyrolysis technique, by adjusting $\frac{[\text{Sn}]}{[\text{Zn}]}$ ratio as 0.7, 1 and 1.3 in the precursor solution. As prepared films are subjected to sulfurization at a temperature of 500 °C for 15 min and its effect on the structure and composition of the films is studied. Sulfurization is carried out under non-vacuum condition inside the spray pyrolysis chamber making it compatible with the deposition technique. Pristine and sulfurized films are analysed using X-ray photoelectron spectroscopy, X-ray diffraction, Raman spectroscopy, UV–Vis–NIR spectroscopy and scanning electron microscopy. X-ray diffraction and Raman spectroscopy suggest the formation of $\text{Cu}_2\text{ZnSnS}_4$ and other binary compounds in the pristine films. Analysis of the sulfurized films indicates that the sulfurization process has brought about a significant change in the composition of the films while improving its crystallinity considerably. Compositional analysis using X-ray photoelectron spectroscopy reveals that substantial amount of indium from the underlying ITO has diffused into the film after sulfurization. However, it is observed that increase in concentration of tin in the film limits the diffusion of indium. Scanning electron microscopic images show the improvement in morphology of the films after sulfurization.

1. Introduction

Copper Zinc Tin Sulfide (CZTS) remains a leading candidate for thin film photovoltaic devices despite the arrival of new materials like conjugated polymers, perovskites, etc. One of the striking features for its high popularity is the relative abundance of its constituents and eco-friendly nature making it a suitable candidate to replace CdTe and CuInSe_2 for low-cost high efficiency thin film solar cells (Suryawanshi et al., 2013). CZTS thin films can be deposited using a variety of methods including vacuum and non-vacuum techniques (Ito, 2015). However, from an industrial point of view, in relation to reducing the cost, a non-vacuum technique such as chemical spray pyrolysis is much more preferable. Chemical spray pyrolysis is a highly reliable non-vacuum technique and has potential for large area coating of thin films with finer control of composition and thickness. It does not require any expensive machinery, thereby enabling significant cost reduction compared to other methods and is ideal for large scale production plants (Perednis and Gauckler, 2005). CZTS thin films can be easily deposited using chemical spray pyrolysis technique (Gurieva et al.,

2013; Rajeshmon et al., 2011; Zeng et al., 2014). Unlike many other techniques, this technique allows direct formation of a homogeneous layer of CZTS over the substrate, thereby eliminating the process of making stacked layers of elementary or binary precursors of copper, zinc and tin. Despite the easiness in fabricating CZTS based thin film solar cells by spray pyrolysis method, the reported power conversion efficiencies are usually lower than the efficiencies reported for devices fabricated using vacuum and other non-vacuum techniques (Sun et al., 2016; Wang et al., 2014). The record efficiency for CZTS based thin film solar cell prepared by spray pyrolysis technique was obtained by Nguyen et al., 2016. They have grown CZTS thin films by spraying an aqueous solution containing $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Sn}(\text{CH}_3\text{SO}_3)_2$ and thiourea; and subsequently annealing the film in sulfur atmosphere. They achieved cell efficiencies up to 8.1%. In our previous report, we have reported CZTS thin film solar cells prepared using spray pyrolysis having a maximum efficiency of 2.5% (Menon et al., 2016). The device was fabricated over ITO coated glass substrate and In_2S_3 was used as the buffer layer. One of the factors limiting the efficiency of our device might be the poor crystallinity of sprayed CZTS. It can be seen in the

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literature that various post-deposition annealing treatments could significantly improve the properties of CZTS thin films (He et al., 2013; Maeda et al., 2011; Pawar et al., 2010; Vanalakar et al., 2014). Hence we ventured into annealing the sprayed CZTS thin films in sulfur atmosphere in order to improve its crystalline properties.

2. Experimental

The chemical spray pyrolysis technique used for the preparation of CZTS consists of spraying an aqueous solution of the precursors onto a heated substrate. Copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$), stannic chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) and thiourea ($\text{CS}(\text{NH}_2)_2$) are used as precursors. The substrate used is ITO coated glass (sheet resistance $\sim 10 \Omega/\square$). The substrate is kept at 350°C and 80 ml of the precursor solution is sprayed over it at the rate of 6 ml/min. The entire process is carried out using an automated chemical spray pyrolysis unit, the details of which are provided elsewhere (Sebastian, 2009). The concentration of tin in the film is varied by varying the precursor ratio. Three different Cu:Zn:Sn:S precursors ratios viz. 1.5:1:0.7:12, 1.5:1:1:12 and 1.5:1:1.3:12 are chosen for preparing tin varied samples. These ratios are achieved by adjusting the molarity of the precursors. The sulfurization of the films is performed inside the spray pyrolysis chamber using powdered sulfur as the source. Basically the process is that, after the spraying process, the films are left on the hot plate at the deposition temperature inside the deposition chamber. The films are then covered using a glass plate and powdered sulfur already taken in a crucible is placed on the hot plate next to the films. The whole arrangement is immediately covered using a glass casing and heated to a temperature of 500°C and annealed for 15 min. After the annealing process, the samples are allowed to cool down naturally. The pristine samples are named as P-Sn(0.7), P-Sn(1.0) and P-Sn(1.3) according to the tin to zinc ratio in the precursor. Similarly, the sulfurized samples are named as S-Sn(0.7), S-Sn(1.0) and S-Sn(1.3).

The pristine and sulfurized films are analysed using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Raman spectroscopy, UV–Vis–NIR spectroscopy and scanning electron microscopy. The composition of the films is obtained from the XPS data acquired using a Kratos Analytical AMICUS spectrometer fitted with the $\text{Mg K}\alpha/\text{Al K}\alpha$ dual anode X-ray source. The structural characterization is done using XRD and Raman spectroscopy. XRD pattern is recorded using a BrukerD8 diffractometer operating at 40 kV and 40 mA. $\text{Cu K}\alpha$ line having wavelength of $1.5405 \text{ \AA}$ is used as radiation source. Raman spectra are recorded using Jobin Yvon LabRAM spectrometer. Argon ion laser of wavelength 514 nm is used as excitation source. Optical characterization is carried out using a Jasco V-570 UV–Vis–NIR spectrophotometer. The surface morphology of the films is analysed using a Carl Zeiss Supra 40VP Field emission scanning electron microscope (FESEM).

3. Results and discussion

3.1. Compositional analysis

The composition of the pristine and sulfurized films are analysed using XPS. Fig. 1 shows the XPS survey scans of the sample P-Sn(0.7) recorded before and after different ‘etch cycles’ (30 s of etching per cycle) using an Ar-ion etching system. Surface composition of the sample is deduced from the core-level spectra as 3.8, 9.6, 8.2 and 20.4% respectively for Cu, Zn, Sn and S. Carbon is found only on the surface as a contaminant. Considerable amount of oxygen is found on the surface (58%) and is present throughout the depth of the sample, though in a lesser quantity. Even though a $\frac{[\text{Cu}]}{[\text{Zn}] + [\text{Sn}]}$ ratio of 0.88 and $\frac{[\text{Zn}]}{[\text{Sn}]}$ ratio of 1.4 was maintained in the precursor solution, the surface of the film has a Zn- and Sn-rich composition while the inner layers have Cu-rich and Sn-poor composition. The percentage of Sn is very less $\sim 3.3\%$ (see

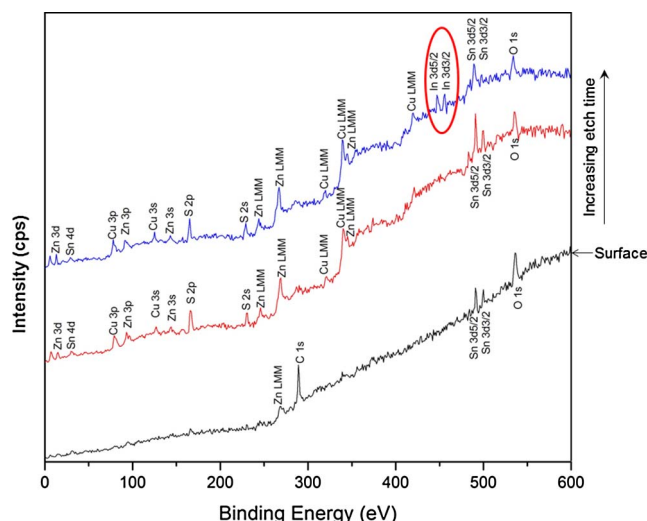


Fig. 1. XPS survey scans of the sample P-Sn(0.7).

Table 1). This indicates that most of the Sn has segregated on the surface. Another interesting observation is the presence of In in the films. The presence of In (0.4%) is found only after the second etch cycle and is due to diffusion from the underlying ITO substrate. The fact that the film thickness is 400 nm and that the 30 s etching removes only a few tens of nanometres of the sample surface, presence of In after second etch cycle suggests that it has been incorporated into much of the CZTS film during the spraying process.

Increasing the tin concentration in the precursor solution has a drastic change in the composition of the films. Even though the tin concentration in the films has increased as expected, there is a sharp decrease in the copper and sulfur concentration. Cu and S concentrations are reduced respectively to 8.9 and 10.3% in case of P-Sn(1.0) while it has even reduced to 6.9 and 6.7%, respectively, for P-Sn(1.3). However, more oxygen is observed to have incorporated into the films (see Table 1). The surface of films is Cu-poor and no segregation of tin is found towards the surface. The incorporation of In is also found to be reduced. For P-Sn(1.0) the quantity of In is 0.2% while for P-Sn(1.3), essentially, no In could be detected. Hence it is apparent that increase in tin concentration in the films limits the diffusion of In from the underlying layers.

Sulfurization of the pristine samples improved the sulfur content in the films. The improvement is much more pronounced in case of S-Sn(1.0) and S-Sn(1.3). However, an overall loss of metallic elements especially, Zn and Sn is observed in all the sulfurized samples. For instance, in case of S-Sn(0.7), Zn and Sn concentration at the surface of the film is reduced to 2.5 and 1.3%, respectively. Even in the inner layer, the atomic concentration of Zn and Sn is reduced to half on sulfurization, compared to the pristine film. The incorporation of In from the underlying ITO is even more pronounced after sulfurization. Considerable amount of In (9.3%) has diffused even into the surface of the film as evident from the XPS survey spectrum measured from the surface (see Fig. 2). Similar observations are also made for S-Sn(1.0) and S-Sn(1.3). The atomic concentration of the elements measured for all the sulfurized samples after 60 s of etching is also presented in Table 1. It may be noted that with increase in tin concentration in the film, there is a sharp decrease in the $\frac{[\text{In}]}{[\text{Sn}]}$ ratio after sulfurization. This may be explained considering the fact that CZTS is a compound semiconductor with inherent point defects (Walsh et al., 2011). As seen from the Table 1, Sn concentration in P-Sn(0.7) is considerably low. This large deviation from stoichiometry will trigger the formation of Sn vacancies (V_{Sn}) in addition to Cu_{Sn} and Zn_{Sn} antisite defects in the film. During sulfurization, owing to the lower formation energy of In_{Sn} antisite (In and Sn are neighbouring elements in the periodic table and has

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