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Structural properties of In_2Se_3 precursor layers deposited by spray pyrolysis and physical vapor deposition for $CuInSe_2$ thin-film solar cell applications

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ABSTRACT

The structural properties of In_2Se_3 precursor thin films grown by chemical spray pyrolysis (CSP) and physical vapor deposition (PVD) methods were compared. This is to investigate the feasibility to substitute PVD process of $CuInSe_2$ (CISe) films by CSP films as precursor layer, thus decreasing the production cost by increasing material-utilization efficiency. Both films of 1 μm thickness were deposited at the same substrate temperature of 380 °C. X-ray diffraction and Raman spectra confirm the formation of γ-In_2Se_3 crystalline phase for both films. The PVD and CSP films exhibited (110) and (006) preferred orientations, respectively. The PVD films showed a smaller full width at half maximum value (0.09°) compared with CSP layers (0.1°). Films with the same crystalline phase but with different orientations are normally used in the preparation of high quality CISe films by 3-stage process. Scanning electron microscope cross-section images showed an important difference in grain size with well-defined larger grains of size 1–2 μm in the PVD films as compared to CSP layers (600 nm). Another important characteristic that differentiates the two precursor films is the oxygen contamination. X-ray photoelectron spectroscopy showed the presence of oxygen in CSP films. The oxygen atoms could be bonded to indium by replacing Se vacancies, which are formed during CSP deposition. Taking account of the obtained results, such CSP films can be used as precursor layer in a PVD process in order to produce CISe absorber films.

1. Introduction

$CuInSe_2$ (CISe) and $Cu(In,Ga)Se_2$ (CIGSe) materials are widely investigated as absorber layers in thin film solar cells. This is mainly due to their high absorption coefficient (10^{-5} cm^{-1}), suitable direct band gap (~1–1.7 eV) and potential low-cost production [1]. Furthermore, CISe and CIGSe solar cells exhibit very good outdoor stability and radiation hardness [2]. In particular, CIGSe thin film solar cells have achieved efficiencies of 20.8% [3]. This efficiency surpasses the best achieved results of multicrystalline silicon and CdTe solar cells [4]. $Cu(In,Ga)Se_2$ films can be deposited by vacuum and non-vacuum methods such as physical vapor deposition (PVD) (e.g. co-evaporation) [5,6], selenization of metal precursor films [7], electrodeposition [8], particulate process (e.g. spin coating, doctor blade) [9–12], and chemical spray pyrolysis (CSP) [13–16].

Non-vacuum deposition methods of CISe have shown significantly lower capital expenditure, reduced material cost and produce devices with considerable efficiencies [14,17,18]. Amongst these methods, the chemical spray pyrolysis deposition has the advantages of low cost equipment, easy scale-up, simple atomization process and temperature control. This deposition is based on the pyrolytic decomposition of small droplets of chloride-based solution sprayed onto a heated substrate under atmospheric conditions [19]. The PVD by co-evaporation method gives the best solar cell efficiencies but poses cost and technological barriers. In this technique, vapors of two different materials are generated simultaneously. These two vapors condense together to form an alloy or a compound. Amongst the different co-evaporation processes, the so-called "3-stage" is essential in obtaining high quality CISe films [20]. This process basically consists of Stage-1: growth of a 1 μm thick In_2Se_3 thin film at low temperature (300–400 °C), Stage-2: these layers are used as precursor during the co-evaporation of copper and selenium, where a Cu-rich film is yielded, Stage-3: indium and selenium are co-evaporated and the film evolves gradually to Cu-poor until the final composition is reached [21]. The In_2Se_3 precursor films used in this process are very important because of i) their direct relationship with the final CISe/CIGSe absorber material quality [22] and ii) its deposition represents around 50% of the total deposition material in a standard 3-stage process [6]. The In_2Se_3 is a III_2–VI_3 semiconductor

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compound that exhibits several phases and crystalline structures (e.g. defected hexagonal, cubic) depending on the deposition conditions.

In this research work, we investigated the feasibility of obtaining CISe films by PVD (e.g. co-evaporation 3-stage) using CSP film as precursor layer by focusing on the structural properties of the In_2Se_3 precursor films obtained from CSP and PVD. This approach could lead to decreased CISe film production cost by increasing the material-utilization efficiency.

2. Experimental details

2.1. Deposition of In_2Se_3 thin films

In_2Se_3 thin films were deposited by PVD and CSP in order to study the difference in the structural properties of the films. A standard 3-stage co-evaporation process uses 1 μm thick In_2Se_3 precursor films deposited at 300–400 °C in order to obtain high quality CISe absorbers [6,22]. For this reason, both PVD and CSP In_2Se_3 layers used in this work were deposited at 380 °C with 1 μm thickness.

2.1.1. Chemical spray pyrolysis process

The In_2Se_3 layers were deposited by CSP on molybdenum coated soda lime glass (SLG) substrates. The CSP films were grown on a molten tin bath at 380 °C. The substrate temperature was monitored by a thermocouple located at the backside of the glass substrate. The details of the CSP setup are described elsewhere [16]. The precursor solutions contain concentrations of 0.0015 M for $InCl_3$ and 0.0055 M for N-N-dimethyl-selenourea (DMSeU) in a 20% volume ethanol aqueous solution. DMSeU was provided in excess of stoichiometry due to the volatile nature of Se at the deposition temperature. The desired pH (4–5) of the solution was achieved by addition of HCl. The total volume of the solution sprayed was 800 ml with a spray rate of 6.5 ml/min with nitrogen as a carrier gas whose flow rate was 1.5 l/min. These parameters yield films of about 1 μm thickness.

2.1.2. Physical vapor deposition process

The In_2Se_3 films of 1 μm thickness were deposited onto Mo/SLG substrates. The elemental fluxes of In and Se were controlled by changing the temperatures of the evaporation sources. A quartz oscillator was used in order to control the evaporation rates and thickness of the film. During the deposition, the substrates were heated by an infrared source. The temperature was monitored by a thermocouple located at the backside of the substrate. The deposition were carried out at a substrate temperature of 380 °C under high vacuum (1×10^{-4} Pa). An effusion cell evaporation source for In and pyrex crucible for Se were used. During the evaporation process, the temperature of In and Se sources were kept at 1010 °C and 285 °C, respectively.

2.2. Thin film characterization

The morphology of the films was observed by scanning electron microscope (SEM)-model JEOL 7600F using an acceleration voltage of 5 kV with a magnification of ×20,000. The average composition of the films was measured by electron dispersive spectroscopy (EDS) using a SEM equipped with an energy dispersive spectrometer SDD SAMx with a resolution of 129 eV, employing a beam current of 0.3 nA and an acceleration voltage of 20 kV. The crystalline quality and orientation were characterized by X-ray diffraction (XRD) using a Cu-Kα radiation (1.541 Å) with a θ/2θ configuration and stepsize of 0.01°. Raman measurements were performed with a Jobin–Yvon T64000 using an argon laser (λ = 514.5 nm) with a probe area around 1 μm^2 for an acquisition time of 5 min. The surface analyses were performed by X-ray photoemission spectroscopy (XPS) in a Kratos Axis Nova with a monochromatic Al K radiation (1486.6 eV) and 160 eV pass energy with an energy step of 0.5 eV. The sputtering was performed for 60 s with an Ar ion beam and beam energy of 300 eV. The C1s signal from adventitious carbon with a binding energy $E_B = 284.6$ eV was used for energy referencing. The peak fit analysis was performed using the CasaXPS software where a linear background was subtracted from the spectra. The spectra were fitted by peaks with a Gauss (60%)–Lorentz (40%) profiles.

3. Results and discussion

3.1. In_2Se_3 thin films grown by PVD

The PVD films were studied by XRD in order to determine their crystalline properties. Fig. 1 shows the diffractogram of PVD-In_2Se_3 thin film grown on Mo/SLG. The films exhibited diffraction peaks corresponding to polycrystalline γ-In_2Se_3. The films have shown (110) orientation with strong (300) and weak (006) lines. This result is in good agreement with the XRD pattern of γ-In_2Se_3 (JCPDS 40-1407) with hexagonal structure [23]. Peaks around 38° and 48° are related to β-In_2Se_3 phase. The peak around 19° does not match with InSe or β-In_2Se_3 phases. The full width half maximum (FWHM) of the (110), (006) and (300) peaks were 0.07, 0.09 and 0.10°, respectively.

The Raman spectrum of the PVD film is shown in Fig. 2a. The main mode located at 149.4 cm^{-1} is related to the formation of a stable polycrystalline γ-In_2Se_3 phase [24]. The Raman modes located around 178 and 203 cm^{-1} are related to both γ-In_2Se_3 [24] and α-In_2Se_3 [25]. The vibrational modes located at around 149 and 227 cm^{-1} appear at the same wave number reported by Wanatabe and Marsilliac et al. [26,27]. This result is consistent with the XRD diffraction measurements.

The surface morphology and cross-section SEM images of PVD In_2Se_3 films are shown in Fig. 3a,b. Surface morphology shows lamellar structures with different grain sizes and also hexagonal grains with 1–2 μm width. These hexagonal grains are related to the growth of the films with (001) orientation. The cross-section image (Fig. 3a) exhibited densely packed columnar structure (~0.8–1 μm). The observed morphologies were attributed to the high surface mobility of adatoms impinging on the surface of the substrate during nucleation stage. The relative chemical composition of the PVD-In_2Se_3 film without considering the oxygen content is shown in Table 1.

The surface of the PVD-In_2Se_3 films was studied by XPS. Fig. 4 shows the O1s core level spectra recorded from un-clean and ion sputtered surface of PVD films. The O1s peak obtained from un-clean surface

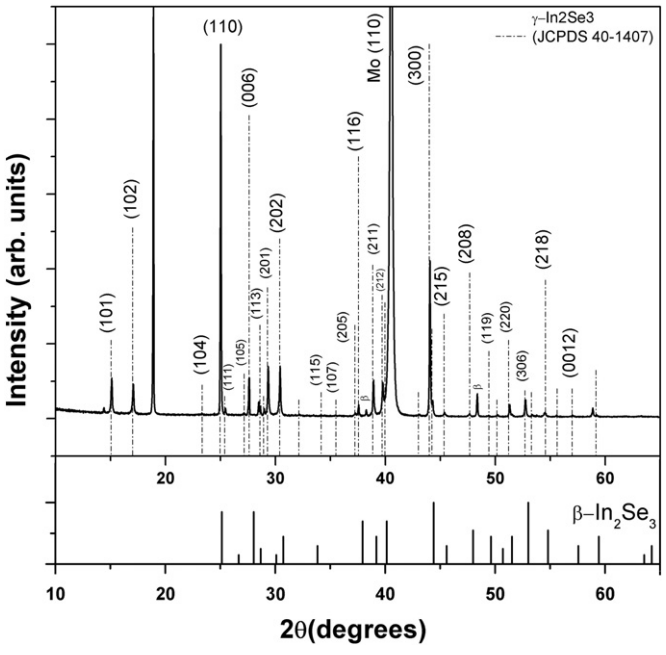

Fig. 1. XRD pattern of the In_2Se_3 film grown by PVD.