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Sb_2S_3 thin films prepared by vulcanizing evaporated metallic precursors

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ABSTRACT

In this study, antimony sulfide (Sb_2S_3) thin films had been grown on Mo-coated glass substrate by evaporating metallic Sb film and subsequent annealing in nitrogen/sulfur (N_2/H_2S) environment. The effects of annealing temperature on phases, morphologies and compositions of thin films and corresponding devices were investigated. It was found that the metallic Sb layer cannot be sulfured completely at annealing temperature of 320 °C, while amount of the formed Sb_2S_3 loss occured at annealing temperature beyond 450 °C. The devices with absorber annealed at 400 °C exhibited the best performance as the film possessed improved morphology and phase structure. This study provides new approach to fabricate Sb_2S_3 thin film and possibilities for large scale industrial application of Sb_2S_3 thin film solar cells.

1. Introduction

Among the metal chalcogenides, antimony sulfide (Sb_2S_3) has attracted attention for the application as promising light-absorbing candidate for these superiorities: (i) it has a reported direct bandgap of ≈1.7 eV [1], (ii) it exhibit high light extinction coefficient ($\sim 1.8 \times 10^5\ cm^{-1}$) [2], (iii) the constituent elements of Sb and S are earth-abundant and environment-friendly. During the past years, some efforts have been devoted to the synthesis of Sb_2S_3 thin films by various techniques such as chemical bath deposition [3–5] and electrodeposition [6] in non-vacuum environment. The main drawbacks of these methods are time-consuming and more importantly, the inevitable incorporation of impurities coming from solvent and carbon or oxide in the air. Therefore, some works on the preparation of Sb_2S_3 films have been done in vacuum environment. For instance, Sb_2S_3 thin films were deposited based on magnetron sputtering of Sb_2S_3 target [1,7] or thermal evaporating Sb_2S_3 pellets [8–10] with high base pressure. Compared with non-vacuum methods, vacuum technique has several advantages such as good uniformity and widely available equipment required for the film deposition. However, as the chalcogen elements always possess high vapor pressure, the concentration of sulfur might be lower than that of the designed one [8]. In this work, Sb_2S_3 thin films are deposited by thermal evaporating metallic Sb and subsequent annealing in nitrogen/sulfur (N_2/H_2S) environment, a method that has hardly been explored for this material to date. Unlike one-step Sb_2S_3 film fabrication method, the sulfuration process of this proposed routine reduces the sulfur vacancies (V_S) which might be detrimental to the performance of device. As the annealing temperature is an important process parameter for the formation of Sb_2S_3 thin film, in this study, we report the characteristic of the fabricated Sb_2S_3 films at different annealing temperature and evaluate their performance in complete solar cells.

2. Experimental details

2.1. Sb_2S_3 thin film deposition

The soda-lime glass slides with area size of $25 \times 70\ mm^2$ were used as the substrate. About 1 μm molybdenum layer was deposited by middle-frequency magnetron sputtering and subsequent with Sb layer deposition by rapid thermal evaporation from 99.99% pure Sb particles (0.5–2 mm). The deposition chamber was pumped to a pressure lower than 1.5×10^{-3} Pa before evaporation. In this study, the thickness of metallic Sb was designed to be around 200 nm. Deposition was carried out at room temperature and lasted for about 30 s. Continuous rotation of the sample holder with 0.6 rad/s during the deposition process was employed to facilitate the homogeneous thickness films. Sb_2S_3 films were obtained by sulfuring the Sb metallic layer in N_2/H_2S environment with a flux ratio of 4:100 at 320–500 °C under 0.3 atm pressure for

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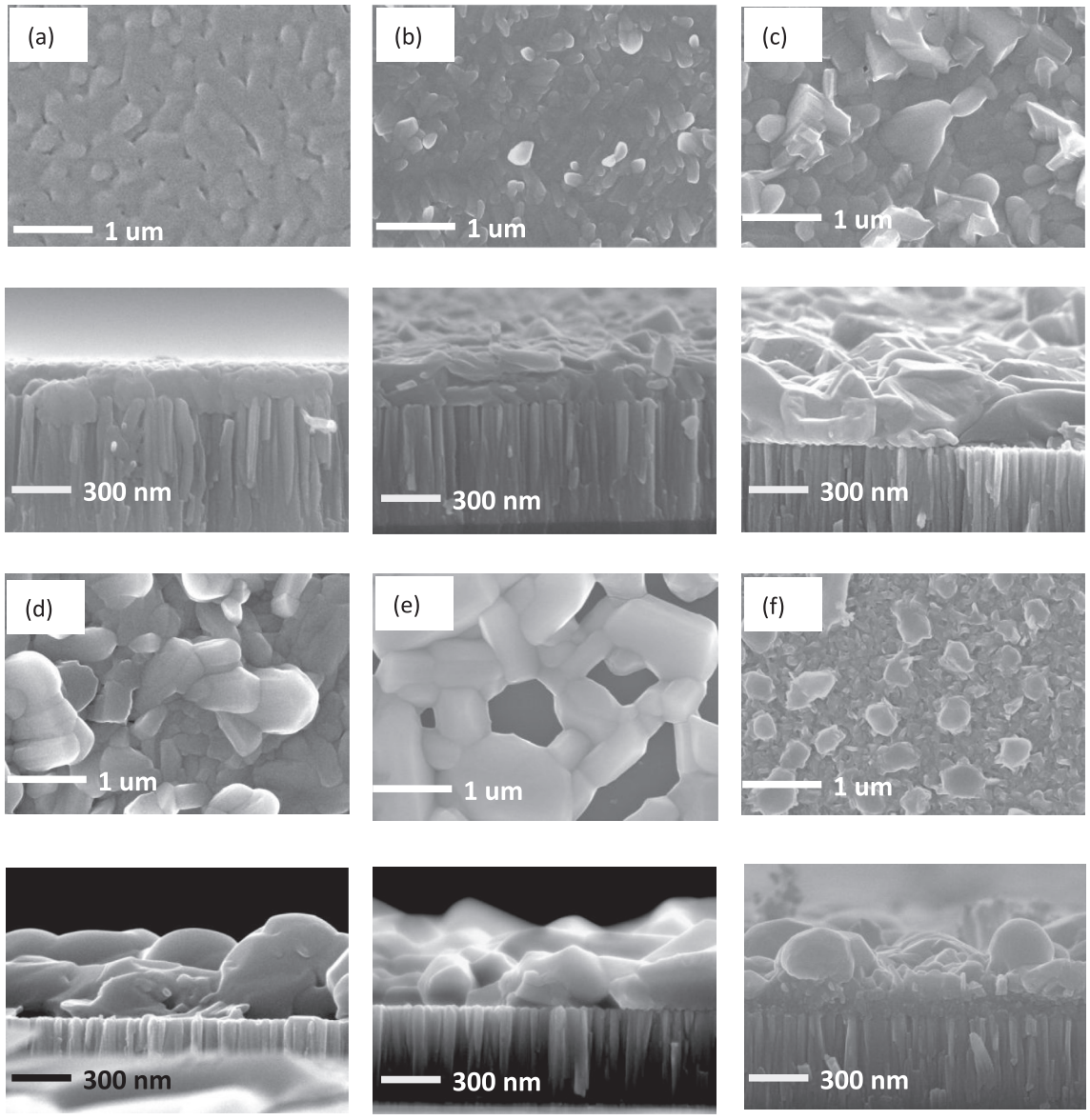

Fig. 1. the surface (upper) and cross-section (lower) microstructure of (a) precursor Sb and samples annealed at different temperature (b) 320 °C, (c) 350 °C, (d) 400 °C, (e) 450 °C, (f) 500 °C.

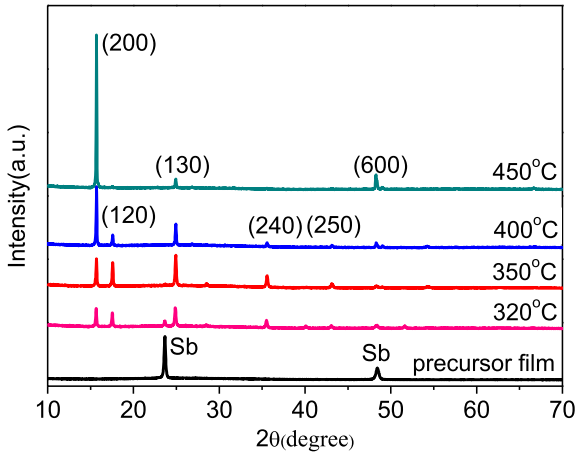

Fig. 2. The xrd patterns of precursor Sb and samples with different annealing temperature.

Table 1
The compositional analysis of antimony sulfide from EDS spectra.

Temperature	Element		
	S(at.%)	Sb(at.%)	S/Sb
320 °C	43.9 ± 2.0%	56.1 ± 2.0%	0.72~0.85
350 °C	58.2 ± 2.0%	41.8 ± 2.0%	1.28~1.51
400 °C	60.7 ± 2.0%	39.3 ± 2.0%	1.42~1.68
450 °C	61.4 ± 2.0%	38.6 ± 2.0%	1.46~1.73

about 20 min. The gas mixture was aerated in the furnace before heating.

2.2. Sb_2S_3 device fabrication

The samples are dipped into a chemical bath to form a thin layer of CdS (~50 nm) and subsequent depositing intrinsic ZnO (50–100 nm) and Al-doped ZnO (300–350 nm) by sputtering by a standard process in the laboratory. The cell size is defined by mechan-

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