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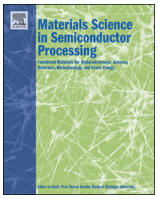

In situ growth of $CuSbS_2$ thin films by reactive co-sputtering for solar cells

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ABSTRACT

$CuSbS_2$ thin films were in situ grown by reactive co-sputtering and the effects of the growth temperature on film composition, structure and morphology were investigated. It is demonstrated that orthorhombic chalcostibite $CuSbS_2$ thin films with uniform morphology, pure phase and grain size over 2 µm can be obtained for growth temperature of 300 °C, while higher growth temperature results in the formation of Cu_3SbS_4 phase and lower growth temperature leads to Sb_2S_3 secondary phase. The grown $CuSbS_2$ film shows an optical absorption coefficient of higher than 10^4 cm^{-1}, an optical band gap of 1.52 eV and p-type conductivity. Solar cell devices with configuration of glass/Mo/$CuSbS_2$/CdS/i-ZnO/ITO/Ag were fabricated and yield power conversion efficiency of 0.52%. The incompatible interfaces including absorber/back contact (the absence of beneficial MoS_2 interface layer) and absorber/buffer layer (unfavorable “cliff”-like conduction band offset) interfaces have been considered as the key factor limiting efficiency.

1. Introduction

In recent years, CdTe and $CuInGaSe_2$ (CIGSe) have been considered as promising absorber materials for thin film photovoltaics (PV) with high conversion efficiency of above 20% [1,2]. However, the scarcity of Te, In, and Ga are major problems limiting the widespread utilization of these devices. Hence, the development of low cost, low toxicity, earth abundant and long-term stability photovoltaic materials is critical for thin film solar cell manufacture. Recently, ternary I-V-VI_2 chalcogenide $CuSbS_2$, which has high optical absorption coefficient between 10^4 and 10^6 cm^{-1} in the visible region [3,4] and a direct band gap of 1.4–1.6 eV [4–6], has aroused interest for application as a promising innovative inorganic absorber material for sustainable and propagable PV due to its non-toxic, low cost, long-term stability and earth-abundant constituents [3]. Furthermore, $CuSbS_2$ has a relatively low melting point of 551 °C [7], indicating that it is suited to crystallization at lower temperatures. Therefore, the exploration of $CuSbS_2$ for photovoltaic application was of great importance based on all these characteristics. Power conversion efficiencies ~ 3% level have been achieved for $CuSbS_2$ thin film solar cells with glass/Mo/$CuSbS_2$/CdS/i-ZnO/ITO/Ag device configuration [8,9]. Besides, 4.70% efficiency has been reach for selenide $CuSbSe_2$ thin film devices, which is the best performance for I-V-VI_2 chalcogenide based solar cells up to now [10].

$CuSbS_2$ thin films can be fabricated by a series of deposition techniques such as thermal evaporation [11–15], RF sputtering [16–18], atmospheric plasma chemical vapor deposition (APCVD) [19], atomic layer deposition (ALD) [20], sulfurization of metal precursor [21–24], spray pyrolysis deposition (SPD) [25–28], hybrid inks [8,29], hot-injection [30–32], hydrothermal [33], solvothermal [34,35], chemical bath deposition (CBD) [36–38], electrodeposition [9,39–41], Spin-coating [42] and drop-casting [43], etc. Deposition of high-quality $CuSbS_2$ thin films is enormously challenging could be attributed to (i) a large number of ternary copper antimony sulfide phases (i.e., Cu_3SbS_3 [16], Cu_3SbS_4 [44], $Cu_{12}Sb_4S_{13}$ [39]) can be formed depending on the process conditions or stoichiometry used during fabrication, and/or (ii) other binary impurities can be synthesized or segregated, such as Cu_xS [30] and Sb_2S_3 [45]. The aforementioned deposition techniques, which all involve the precursors preparation followed by a high temperature sulfurization, may easily introduce impure phase into the film and increase the complexity for large scale applications. It is necessary that a large area deposition process and direct “one step” should be applied in the field of large scale production of thin film PV. Reactive co-sputtering deposition techniques, as a suitable technique for this task, can not only simply provide control on deposition rate, thickness and film composition by just adjusting the deposition time and ratio of the powers applied to the metal targets, but also applicable for large area, successive and multi-component film deposition with relatively low cost [46]. In addition, the phase of material can be regulated in real

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time to induce the growth of a small amount of impurities, defects and secondary phases in the film through this method [47].

In this work, we present a Reactive co-sputtering deposition techniques for the in situ growth of $CuSbS_2$ thin films onto Mo-coated glass substrates for solar cells. The effects of the growth temperature on film composition, structure and morphology were investigated. Solar cell device with configuration of glass/Mo/$CuSbS_2$/CdS/i-ZnO/ITO/Ag was also fabricated and yielded a conversion efficiency of 0.52%.

2. Experimental

$CuSbS_2$ films were deposited onto Mo-coated glass substrates (40 mm × 40 mm) by reactive co-sputtering with two metal targets of Cu (purity: 99.99%) and Sb (purity: 99.99%) in the mixed Ar/H_2S working gas at different growth temperatures (200–350 °C). The metal targets were 5 mm in thickness and 60 mm in diameter. Before sputtering, the chamber was pumped down to lower than 1×10^{-4} Pa. The flow rate of argon (purity: 99.999%) and hydrogen sulfide (purity: 99.9%) were 30 and 10 sccm, respectively. The working pressure is set at 0.5 Pa. The sputtering source was operated using metallic Cu and Sb targets, by two independent RF power of 120 W and 80 W, respectively. The sputtering time was 15 min. The $CuSbS_2$ solar cells were completed using the CBD 50 nm CdS buffer layer, the RF-sputtering 50 nm intrinsic ZnO (i-ZnO) and the DC-sputtering 300 nm ITO window layer. Each device had a total area of approximately 0.45 cm^2 defined by mechanical scribing.

The composition of films was investigated by X-ray fluorescence (XRF, Shimadzu XRF-1800). The morphology of the thin films were studied by scanning electron microscopy (SEM, FEI Quanta-200). The phase structure was measured by both X-ray diffraction (XRD, Rigaku3014) patterns and Raman spectra (Raman, LabRAM HR800, 520 nm). The elements state of the $CuSbS_2$ films were analyzed by X-ray Photoelectron Spectroscopy (XPS, KAlpha). Optical properties of the films were measured using an UV–Vis–NIR spectrophotometer (Hitachi U-4100). The electrical properties of samples were measured using Hall effects measurement (HMS-3000/0.55T). Current density-voltage (*J-V*) characterization for PV structures were performed using an AM 1.5 solar simulator (NEWPORT, 100 mW/cm^2).

3. Results and discussion

The elemental composition of the grown thin films at different growth temperature was determined by XRF measurements and shown in Table 1. It was observed that the composition of the deposited films is sensitive to the growth temperature. The Cu/Sb radios of the films increases 0.48–2.70 as the growth temperature increased from 200 °C to 350 °C, which may be related to the high volatility of Sb_2S_3 phase [3,11]. For growth temperature of 200 °C and 250 °C, atomic ratio Cu/Sb is far lower than 1, which is close to 1 and shows slightly Cu-poor composition at growth temperature of 300 °C. Cu/Sb rises sharply to highly Cu-rich when the growth temperature reaches 350 °C, suggesting a significant loss in Sb. The S/(Cu + Sb) radios were observed to be reduced with increasing in growth temperature from 200 °C to 300 °C, and then remain at 1.1–1.2, showing a slightly S-rich composition. According to previous report, Cu-poor and S-rich composition is required for high efficiency I-V-VI_2 chalcogenide based solar cells [3], the optimal growth temperature is 300 °C.

Table 1
Elemental composition of the $CuSbS_2$ films prepared at different growth temperature.

S.No.	growth temperature	Atomic percent (at%)			Ratio	
		Cu	Sb	S	Cu/Sb	S/(Cu + Sb)
1	200 °C	13.34	28.06	58.60	0.48	1.41
2	250 °C	15.90	28.94	55.15	0.55	1.22
3	300 °C	23.05	24.25	52.70	0.95	1.11
4	350 °C	33.80	12.52	53.68	2.70	1.15

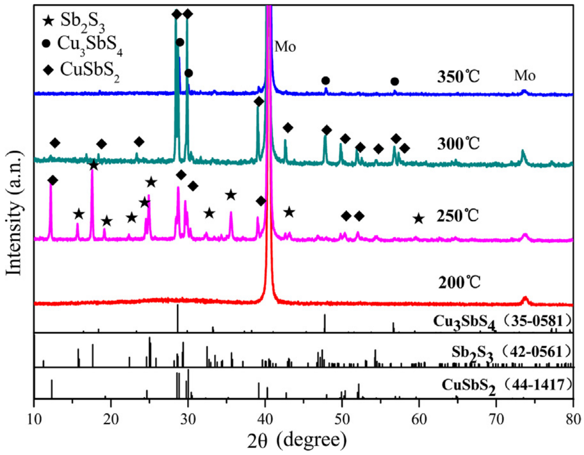

Fig. 1. XRD diffraction patterns for $CuSbS_2$ thin films deposited at growth temperature of 200, 250, 300 and 350 °C.

Fig. 1 shows XRD of the grown thin films at different growth temperature. It is obvious that the phase formation was influenced strongly by the growth temperature. No diffraction peaks of $CuSbS_2$ can be observed in the thin films grown at 200 °C except for the peaks from substrate, indicating an amorphous state of the film. For growth temperature of 250 °C, the samples shows orthorhombic chalcostibite $CuSbS_2$ (JCPDS No 44-1417) phase with segregated Sb_2S_3 [11,48] (JCPDS No 42-1393), which explains the atomic ratio of Cu/Sb far lower than 1. For growth temperature of 300 °C the sample shows only orthorhombic $CuSbS_2$ phase without observable secondary phases. Two intense and sharp peaks at about 28.4° and 29.9° from (111) and (301) reflections can be observed, revealing good crystallinity. For growth temperature of 350 °C, the samples showed main phase of the famatinite Cu_3SbS_4 [34,43] (JCPDS No 35–0581), which leads to the high Cu/Sb value of 2.7 as show in Table 1. Therefore, 300 °C again can be considered as the most suitable growth temperature.

Fig. 2 shows SEM images of surface morphologies of the $CuSbS_2$ thin films prepared at different growth temperatures. The films grown at 200–300 °C shows compact and uniform surface (Fig. 2(a-c)). And it can be seen that the grain boundaries become clear and grains size become larger gradually with the increasing in growth temperature, suggesting an improvement in crystallinity. Particularly at growth temperature of 300 °C as shown in Fig. 2(c), the film consisted of dense large grain with size of larger than 2 μm, which is beneficial to high efficiency of the thin film solar cells according to the experience in CIGSe photovoltaics [49]. As the growth temperature was further increases to 350 °C, the film surface microstructure (Fig. 2(d)) has changed dramatically, showing cluster-like morphology consisting of belted-particles. Combined with XRF and XRD analysis, this can be related to phase transformation of the films from $CuSbS_2$ to Cu_3SbS_4. Based on the above composition, structure and morphology characterizations, one can clearly find that growth temperature of 300 °C can yield orthorhombic $CuSbS_2$ thin films with slightly Cu-poor and S-rich composition, compact and uniform morphology, and good crystallinity, which was employed for further characterizations and device fabrication.

Fig. 3(a) displays the cross-section of the films prepared at growth temperature of 300 °C. It is obviously that film has a thickness of 1 μm and shows large columnar grains but a fine grain layer at the bottom. No voids in the $CuSbS_2$ absorber or at the absorber/Mo interface can be observed. The interface layer MoS_2, which is usually found in CIGSe and Cu_2ZnSnS_4 (CZTS) cases, also cannot be observed. This suggests the interface reactions of Mo with absorber and/or chalcogen from the reactive annealing, which occur in CIGSe and CZTS cases, is not