The Effect of Annealing Steps of Spin Coated Sb_2S_3 Film in Planar Structure Solar Cells

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Abstract:

The inorganic Sb2S3 thin-film solar cells have increasing attention due to their merit features, which are suitable for solar cell applications. The performance of solar devices is varied based on different conditions of film deposition. The annealing temperature is an important factor in the spin-coated Sb2S3 layers because it changes from amorphous to crystalline during the preparation. Therefore, the present work was done by a step-annealing process of Sb2S3. Herein, Sb2S3 precursor was prepared by using 1 mmol of Sb2S3 and 1.5 mmol of thiourea in 1 ml of 2-methoxyethanol and it was spin-coated at 4000 rpm on com-TiO2/FTO. Just after coating, the cells were annealed in two different conditions. For the first condition, the coated Sb2S3 was pre-heated inside the tube furnace at 160^o C for 1 minute, then again annealed at 280 oC for 10 minutes. In the second condition, the Sb2S3 was annealed in a single step at 280 oC for 10 minutes. All these annealing processes have proceeded under N2 stream. In the cell with a two-step annealing, the desired phase was synthesized and photo-generated electron-hole pairs effectively converted. By improving the photovoltaic parameters, the power conversion efficiency (PCE) of 1.76% was achieved in a configuration of FTO/com-TiO2/Sb2S3/P3HT/Ag.

Keywords: absorption, crystallization, efficiency, step-annealing, Sb_2S_3

1. Introduction

Many metal chalcogenides such as antimony sulfide (Sb_2S_3), lead sulfide (PbS), and cadmium sulfide (CdS) have been widely investigated as a light absorber layer in solid-state solar cells. Among them Sb_2S_3 has been successfully used for various merits such as high absorption coefficient, wide bandgap (1.2-1.7 eV), air/moisture stability, environmentally friendly, abundant in nature, low melting point and with an approximate thickness of 1 μm can absorb almost 95% of the solar radiation [1-2].

Because of its low melting point (~550 ^oC), high crystalline Sb_2S_3 films can be synthesized in low-temperature conditions (<350 ^oC). However, most of the studies indicated that as-prepared Sb_2S_3 films are in amorphous form. Therefore, an additional annealing process is required with inert gases/air for crystallization [3-4]. X. Wang et al. found that the crystallization process was started at 250 ^oC, the crystallinity was increased up to 300 ^oC and above 300 ^oC, and there were no changes in the XRD pattern and weight loss of the powder, which confirmed the amorphous to crystalline nature of Sb_2S_3 [5]. At 280 ^oC, the Sb_2S_3 film shows crystalline nature while the amorphous nature exhibits less temperature condition. The crystalline Sb_2S_3 has a wide range of spectrum in the visible region.

In our system, the Sb_2S_3 film was fabricated in two-step annealing process. The Sb_2S_3 precursor was deposited on the compact TiO_2 layer to form the uniform Sb_2S_3 films. Because non-optimal

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adhesion prevents direct coating of Sb_2S_3. Our study shows that the step-annealing process improves the film quality.

2. Methodology

A 75 μl of Titanium (IV) isopropoxide (TTIP) was added to 50 μl of di-ethanolamine and 910 μl of butan-1-ol to prepare TiO_2 precursor. It was deposited on the cleaned Fluorine-doped tin oxide (FTO) by spin coating at 3000 rpm for 30 s. Then, the coated cells were sintered inside the furnace at 500^o C for 1 h. The Sb_2S_3 precursor solution was prepared by adding 228 mg of Antimony trichloride ($SbCl_3$) and 114 mg of thiourea (TU) in 1 ml of 2-Methoxyethanol. The prepared solution was spin-coated on TiO_2 layer at 4000 rpm for 30 s. The coated Sb_2S_3 cells were synthesized in a step-annealing process. The coated Sb_2S_3 films were heated inside the tube furnace at 160^o C for 1 min and again annealed at 280^o C for 10 mins under N_2 gas. Another set of cells were fabricated by direct annealing inside the tube furnace at 280^o C for 10 mins under N_2. Then, the P3HT solution was spin-coated on Sb_2S_3, which was prepared by dissolving 20 mg of P3HT in 1 ml of chlorobenzene. Finally, 70 nm of silver (Ag) was deposited by the thermal evaporation technique. This experiment was repeated 6 times. Optical absorption spectra were obtained using Shimadzu 2450 UV–VIS spectrophotometer. IPCE curves were measured as a function of wavelength from 300 to 800 nm using the Bentham PVE300 photovoltaic Device Characterization System. Cells were fabricated with an effective area of 0.18 cm^2 using a mask. Current–Voltage measurement and electrochemical impedance spectroscopy (EIS) of each cell were taken by using Metrohm Autolab under the illumination of 100 mW cm^{-2} with AM 1.5 spectral filter.

3. Results and Discussion

The Sb_2S_3 films in different annealing conditions were deposited on a compact TiO_2 layer to form the uniform Sb_2S_3 films. The UV-Vis absorption spectra of Sb_2S_3 films are shown in figure 1(a). At 160^o C, the cell shows nearly the absorption of TiO_2, which means the active elements of Sb_2S_3 was fewer. By increasing annealing temperature, the crystallinity of the film is increased. Therefore, by heating in the second step, the crystallite Sb_2S_3 was produced and absorption was increased. Even though the cell with a direct annealing process shows a higher range of absorption than the cell in two-step annealing, the photovoltaic performance was improved in the cell with two-step annealing. The defect also can increase the absorption in some conditions but which leads the low performance [2]. By direct heating (280^o C), decomposition occurs and surface oxide is produced. However, at insufficient (low) temperature of Sb_2S_3 is resulted in poor crystallinity of the films. The Sb_2S_3 films show a considerable absorption range in 500-800 nm. We can conclude that Sb_2S_3 films absorb nearly all the visible light with proper annealing.

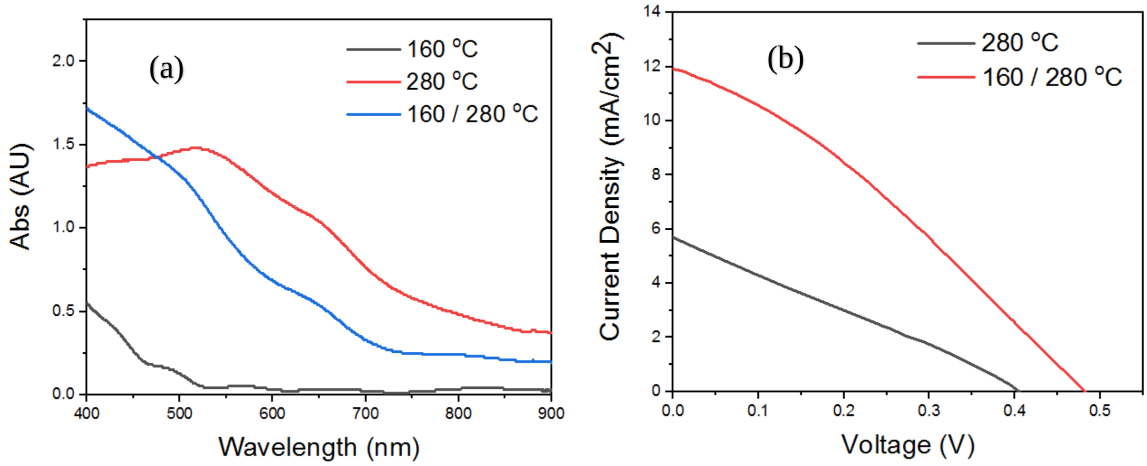

Figure 1: The UV-Vis absorption spectra (a) and J-V characteristic curves (b) of Sb_2S_3 in different annealing conditions.

The thickness of the Sb_2S_3 layer was calculated using Beer-Lambert law and absorbance spectra as 34, 194, and 180 nm for 160, 280, and 160/280 °C respectively. Figure 1(b) shows the J-V characteristic curves of the cell with direct and step annealing. The photovoltaic parameters are summarized in table 1, including open-circuit voltage (Voc), short-circuit current (Js), fill factor (FF), power conversion efficiency (PCE), series resistance (Rs), and charge transfer resistances (R_1 and R_2). The photovoltaic parameters are improved by the step-annealing process, which leads to a good PCE of 1.76%.

Table 1: The photovoltaic parameters of Sb_2S_3 in different annealing conditions.

Annealing steps temp (°C)	Voc (mV)	Jsc (mA/cm²)	FF (%)	PCE (%)	Rs (Ω)	R_1 (Ω)	R_2 (Ω)
280	405.1	5.9	26.1	0.62	16.8	20.8	98.2
160 / 280	481.6	11.9	30.8	1.76	18.4	8.04	56.1

Figure 2(a) shows the EQE spectra of the devices. The EQE value exhibited a higher range of response for the two-step annealing process than the single-step, which attributes the higher Jsc of the device. Here, P3HT absorbs light in a wavelength range of 550-600 nm. But, the generated charge carriers are not completely transferred to either the photo-anode or counter electrode. Therefore, a lower EQE is revealed in a specific wavelength range for both devices.

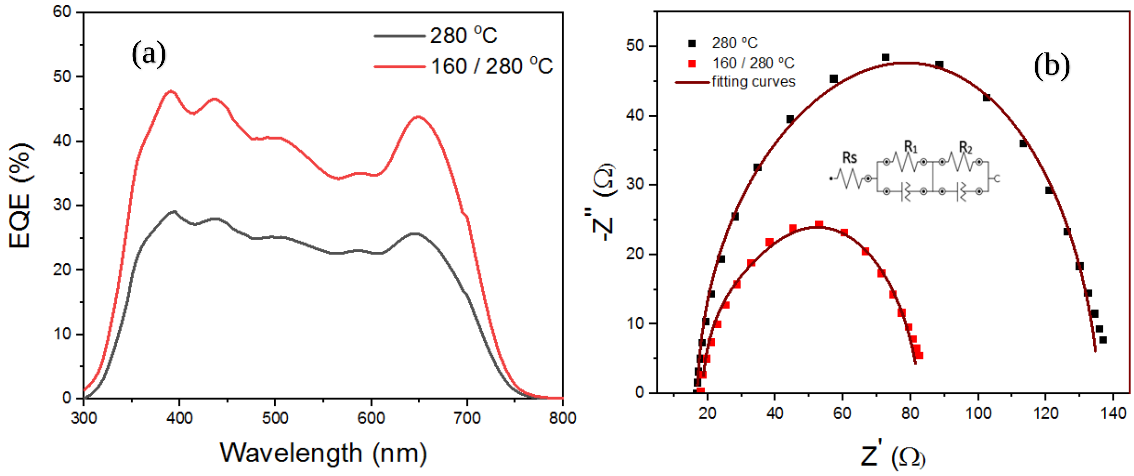

Figure 2: The IPCE spectra (a) and EIS curves (b) of Sb_2S_3 in different annealing conditions.

The EIS spectra of each device are given in figure 2(b) with a fitted equivalent circuit. The R_1 and R_2 associated with charge transfer from the active layer of the devices possess on the phases of TiO_2/Sb_2S_3 and Sb_2S_3/HTM. The device with a step-annealing process exhibits a lower R_1 and R_2 while the series resistance (Rs) is high. Here the Rs is overcome by Rsh. Therefore, the device with a step-annealing process showed an enhanced device performance.

4. Conclusion

From our results, it was found that the direct annealing process of Sb_2S_3 by spin coating has a negative effect on solar cell performance. By proper annealing process, the quality of the film (optical and electrical properties) can be improved, which could enhance the PCE. The device with a step-annealing process improved the PCE nearly 2.8 times higher than direct-annealing.

5. References

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