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Sb_2Se_3 thin film solar cells in substrate configuration and the back contact selenization

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ABSTRACT

In this work, antimony selenide (Sb_2Se_3) thin films were prepared by co-evaporation of Sb_2Se_3 and selenium (Se) sources on molybdenum (Mo)-coated soda lime glass. Solar cells were fabricated in the substrate configuration of Ag/ITO/ZnO/CdS/Sb_2Se_3/Mo/Glass. The [hk1] preferred orientation grain was found to be beneficial to higher performance solar cells because of its special one-dimensional crystal structure. Furthermore, a Mo selenization process prior to the Sb_2Se_3 deposition was introduced to improve the Sb_2Se_3/Mo interface. Material characterization and device physics analysis revealed that the formation of $MoSe_2$ due to the Mo selenization enhanced the [221] orientation preference of the following Sb_2Se_3 and improved the quality of heterojunction, leading to a significant increase in open circuit voltage (V_{OC}) and fill factor (FF). The champion solar cell showed a conversion efficiency of 4.25% with a V_{OC} of 427 mV and a FF of 58.15%.

1. Introduction

Antimony selenide (Sb_2Se_3), as a simple, non-toxic, highly earth-abundant and low-cost material with proper band gap (1.0–1.2 eV) and high absorption coefficient ($>10^5$ cm^{-1}), is a promising alternative light absorber for photovoltaic application [1–4]. Sb_2Se_3 has a special one-dimensional ribboned crystal structure. The ribbons stack through covalent bonds in the direction along the ribbon, while they are held together via non-bond forces in the direction cross the ribbon [5,6]. While the oriented ribbons stand vertically on the substrate, photo-generated carriers would transport efficiently along the one-dimensional ribbons, yielding high mobility and low recombination rate. The theoretical conversion efficiency of Sb_2Se_3 thin film solar cells can reach as high as 25% [7,8]. In addition, numbers of technological methods can be used to prepare the Sb_2Se_3 films with single and stable phase. Choi *et al.* reported that Sb_2Se_3 was prepared by spin-coating with a single source precursor solution and Sb_2Se_3-sensitized solar cells were fabricated with an efficiency of 3.21% [2]. Solar cell sensitized by electrodeposited Sb_2Se_3 was reported to yield an efficiency of 2.1% [3]. Tang's group demonstrated hydrazine-based solution processed Sb_2Se_3/TiO_2 thin film solar cells and achieved a conversion efficiency of 2.26% [9]. At the same time, conventional thermal evaporation and rapid thermal evaporation were used to deposited Sb_2Se_3 thin films, and the corresponding superstrate Sb_2Se_3/CdS heterojunction solar cells showed the highest efficiency of 5.6% [10,11]. Recently, our group reported that superstrate Sb_2Se_3/CdS thin film solar cells with the Sb_2Se_3 light absorber deposited by thermal co-evaporation from Se and Sb_2Se_3 powder sources achieved an efficiency of 3.47% [12].

However, most of these work focused on the Sb_2Se_3-based thin film solar cells with superstrate structure due to the good adhesion and ohmic contacts for Sb_2Se_3 layer. From the perspective of scientific research, the substrate configuration, as an alternative structure, allows the properties of absorber layer and the corresponding heterojunction to be optimized independently. In addition, solar cells on opaque substrates, such as flexible metal or plastic foils, have to be in the substrate configuration. Unfortunately, research on substrate structural Sb_2Se_3 thin film solar cells is very limited except the report by Chen et al., in which the Sb_2Se_3 absorber layer were thermal-evaporated on fluorine-doped tin oxide (FTO) glass. The device achieved an efficiency of 2.1% with a V_{OC} of 354 mV and a FF of 33.5% [13]. The low fill factor might be resulted from the poor contact of Sb_2Se_3 and FTO back contact layer. Very recently, Zhu's group fabricated substrate structure Sb_2Se_3 thin film solar cells with an efficiency of 3.47%, in which the Sb_2Se_3 absorber layers were prepared by sputtering Sb and post-

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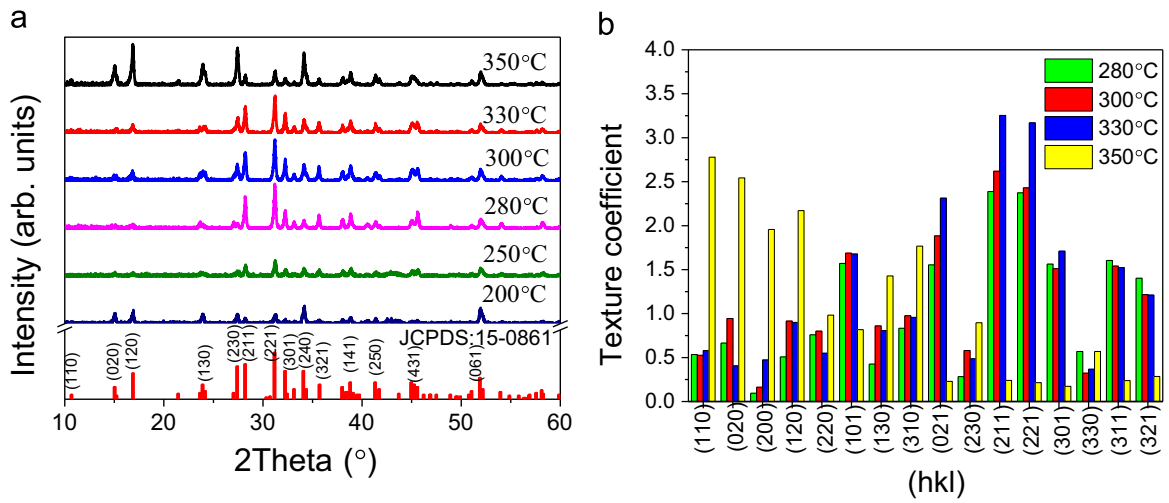

Fig. 1. (a) XRD patterns and (b) the texture coefficients of the diffraction peaks of the Sb_2Se_3 thin films deposited on Mo-coated glass at different substrate temperatures.

selenization process [14].

In this work, Sb_2Se_3 thin film solar cells with a substrate structure of Ag/ITO/ZnO/CdS/Sb_2Se_3/Mo/Soda-lime glass (SLG) were fabricated. Mo layer, acting as the back metal contact, consists of two stacked films deposited by sputtering at low and high working pressures, achieving both high electrical conductivity and good adhesion to SLG [15]. The Sb_2Se_3 layers were deposited by co-evaporation of Sb_2Se_3 and Se powders. The influence of substrate temperature on Sb_2Se_3 thin films as well as device performances were investigated systematically first. Forming a $MoSe_2$ layer on Mo back contact by preheating the Mo layer in a Se atmosphere improved the performance of the substrate Sb_2Se_3 thin film solar cells. Such effect was then comprehensively investigated by the use of Raman scattering and capacitance-voltage (C-V) measurement etc.

2. Experimental

2.1. Deposition of Sb_2Se_3 thin films and device fabrication

The bilayer Mo was deposited in an argon (Ar) atmosphere by direct current sputtering excited with a discharge power of 1200 W. Ar pressure of 5 Pa was used for deposition of first Mo layer and 0.2 Pa for the second layer (top layer) [14]. For the selenization of the surface of Mo back contact, the Mo-coated glass substrates were treated in a Se vapor atmosphere before the deposition of Sb_2Se_3 layers. Different treatment durations ranging from 10 to 40 min and different sample temperatures from 450 °C to 640 °C were used in the selenization process, and Se source was kept at 147 °C during the treatment. The Sb_2Se_3 layers were prepared by co-evaporation of Sb_2Se_3 and Se powders with Knudsen source effusion cells in a co-evaporation system at different substrate temperatures ranging from 200 °C to 350 °C [16]. The thickness of all Sb_2Se_3 films was intentionally maintained at around 500 nm by varying the deposition time. Note that it was difficult to deposit Sb_2Se_3 films when the substrate temperature was higher than 350 °C due to the too high sublimation rate of Sb_2Se_3 from the substrate. Then a 60 nm thick cadmium sulfide (CdS) layer was deposited by chemical bath deposition (CBD) method to form the Sb_2Se_3/CdS heterojunction. A 80 nm thick intrinsic zinc oxide (ZnO) and a 200 nm thick indium tin oxide (ITO) layer were deposited by magnetron sputtering as the window layers. Silver grids with thickness of about 200 nm were evaporated to complete the thin film solar cell, acting as the front electrode.

2.2. Measurement and characterization

The crystal structures of Sb_2Se_3 were characterized by X-ray diffraction (XRD) with Cu Kα1 (1.54056 Å) radiation (Bruker D8 Advance). Lattice vibrations of the films were characterized by Raman spectroscopy at room temperature (Horiba JobinYvon, LabRAM HR800, 532 nm excitation wavelength). The surface morphology and cross-sectional images of Sb_2Se_3 thin films were taken by scanning electric microscopy (SEM, FEI NOVA NANOSEM 450). A Horiba glow discharge spectroscopy (GDS) tool was used to evaluate the elemental content profile along the growth direction in the solar cells. The current density-voltage (J-V) measurement of Sb_2Se_3 thin film solar cells was performed using an AM1.5 solar simulator equipped with a 300W Xenon lamp (Model No. XES-100S1, SAN-EI, Japan). External quantum efficiency (EQE) was measured using a Crowntech Qtest station equipped with a 150W xenon light source, a lock-in amplifier and an integrating sphere. Capacitance-voltage (C-V) measurement was performed on Agilent B1500A Semiconductor device analyzer in darkness at room temperature.

3. Results and discussion

3.1. The influence of substrate temperatures on Sb_2Se_3 films and solar cells

We first employed XRD to identify the crystal phases in the co-evaporation deposited Sb-Se thin films on the Mo-coated glass. Fig. 1a showed the XRD patterns of the six Sb-Se thin films deposited by thermal evaporation at different substrate temperatures ranging from 200 °C to 350 °C. All the diffraction peaks of the six thin films were identified and indexed to the orthorhombic Sb_2Se_3 (JCPDS No. 15–0861) and no diffraction peaks of other impurity phases were observed. The peaks of samples deposited at 200 and 250 °C were very weak. It was observed that the films obtained at the substrate temperatures of 280, 300 and 330 °C exhibit a strong (221) peak and there was no obvious difference in the XRD patterns between these three samples. As the substrate temperature increased to 350 °C, the intensity of (221) peak was weakened while the intensity of (120) peak got stronger. To quantitate the difference of orientations between the samples deposited at different substrate temperatures, the texture coefficient (TC) of diffraction peaks of samples was calculated based on the following equation [17]:

$$TC_{hkl}=\frac{I_{(hkl)}}{I_{0(hkl)}}/\left(\frac{1}{N}\sum_{N}\frac{I_{(hkl)}}{I_{0(hkl)}}\right) \quad (1)$$