EFFECT OF SnS BUFFER LAYER ON SOLUTION PROCESS PREPARED Cu_2ZnSnS_4 SOLAR CELLS

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The effects of SnS buffer layers on the interfacial morphology, electrical model, and photovoltaic properties of solution-prepared CZTS devices were examined. Two SnS buffer layers were prepared and compared. The CZTS device that was fabricated on the as-coated SnS had many interfacial voids. By contrast, the annealed SnS layer markedly improved the CZTS quality by eliminating the voids at the CZTS–MoS_2 interface. An additional capacitance–resistance circuit in parallel that was responsible for the interfacial defects was required to fit the admittance spectrum of the CZTS device prepared on the as-coated SnS. The efficiency of the CZTS solar cell prepared on the annealed SnS was as high as 8.8%, open-circuit voltage was 570 mV, short-circuit current was 24.08 mA/cm^2, and fill factor was 64.5%. The open-circuit voltages and fill factor increased 43% and 72%, respectively, when the interlayer changed from the as-coated SnS to the annealed SnS.

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1. Introduction

Cu_2ZnSnS_4 (CZTS) has emerged as one of the most promising absorber materials for thin-film solar cells because it contains earth-abundant, low-cost, and nontoxic elements [1]. Recently, CZTS photovoltaics have reached a record conversion efficiency of 12.6% [2]. To further enhance the efficiency, optimizing the CZTS/Mo back contact properties has been identified as one of the key tasks. Mo has been widely adopted as a substrate for CIGS and CZTS because it is conductive and can endure of high-temperature processes. Moreover, the formation of a thin $MoSSe_2$ interlayer relaxes the interfacial stress that enhances the interfacial quality. However, the decomposition reaction of CZTS at the Mo/CZTS interface is unavoidable and severely deteriorates the interfacial coherency and phase purity [3]. Therefore, the insertion of interfacial layers between the CZTS and Mo back contact has been demonstrated to effectively improve the device efficiency by reducing the interfacial reaction [4]. Nevertheless, the introduction of interfacial layers has also been reported to cause some problems. For example, a TiN interlayer enhanced the cell efficiency, but created a high series resistance that reduced the fill factor [5]. A TiB_2 interlayer was also shown to enhance the interface morphology and reduce the voids, but the open-circuit voltage was decreased [6]. In addition, a silver layer improved the cell efficiency but degraded the crystallinity of the CZTS [7]. Basically, inserting a buffer layer should avoid the formation of a pair of back-to-back p–n contacts and chemical reactions with the absorber. To this end, we previously presented that the insertion of a very thin SnS buffer layer improved the adhesion of the CZTS absorber, but that research focused on layered metallic precursors deposited through a vacuum process [8]. In the

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current study, we propose that an annealed SnS buffer layer is an appropriate buffer layer for a CZTS precursor that was prepared by a solution process. The use of a proper SnS buffer markedly improved the efficiency of the solar cell from 5.1% to 8.8%.

2. Experimental

A SnS precursor was synthesized using a 2-Methoxyethanol (EGME) solution process. Tin (II) chloride ($SnCl_2$) and thiocarbamide (CH_4N_2S) were dissolved in an EGME solution, and the transparent SnS solution was dropped onto a Mo-coated soda lime glass and spin-cast at 10000 rpm. The SnS precursor was dried at 210 °C for 10 min to remove organic impurities. Subsequently, two SnS samples were prepared. One was the as-cast SnS and the other was heat treated at 350 °C. The solution process used to fabricate the CZTS absorber was presented previously [9]. Copper (II) chloride ($CuCl_2$), zinc(II) chloride ($ZnCl_2$), $SnCl_2$, and CH_4N_2S were dissolved in the EGME solution. After these completely homogenized, a clear yellow solution was formed. A CZTS precursor was prepared by dropping the solution onto SnS and spin-casting at 5000 rpm. The as-prepared CZTS was dried at 210 °C to remove the residual solvent. Subsequently, the CZTS precursor was sulfurized at 520 °C in a sulfur atmosphere to form a CZTS thin film. After sulfurization, a CdS layer, an undoped ZnO layer, an Al–ZnO layer, and a Ni–Al electrode were sequentially deposited on the CZTS absorber. The morphology of the CZTS thin films were characterized using scanning electron microscopy (SEM, JEOL 6500F at 15 kV), and the element ratio was measured by energy dispersive X-ray spectroscopy (EDS, JEOL JSM-6480LV). The admittance measurements were performed by using an Agilent 4294A precision impedance analyzer with the amplitude set to be a constant 25 mV with no applied bias and the frequency range was 40 Hz to 1MHz. The instrument control, data acquisition, and analysis were performed using ‘ZView’ software. The cell parameters were measured by the Industrial Technology Research Institute (ITRI), Taiwan. The device efficiency was measured using a solar simulator (Wacom WXS-220S-L2), which met the requirements of IEC60904-3 and JIS-C 88904-3 AM 1.5G global, and a Keithley 2400 SourceMeter (certificated by AIST, No. P14002).

3. Results and discussion

Cross-sectional SEM images of the as-coated CZTS thin films on the as-coated and annealed SnS buffer layers are depicted in Fig. 1(a) and (c), respectively. The SnS buffer layers in both samples exhibited a thickness of approximately 300 nm. After sulfurization at 520 °C, the SnS layers were invisible, the thickness of the CZTS films was 1 μm, and the grain size was 1 μm throughout the films, as shown Fig. 2 (b) and (d). Table 1 shows the elementary ratio of the two CZTS absorbers. Cu-poor and Zn-rich stoichiometry was desired for both of the CZTS films. The MoS_2 interlayer between Mo and CZTS was approximately 100 nm. The CZTS that was prepared on the as-coated SnS had many voids at the CZTS–MoS_2 interface, which was similar to the properties of a CZTS absorber without a buffer layer. The sulfurized CZTS fabricated on an annealed SnS buffer layer showed suitable adhesion with Mo, and no void was observed.

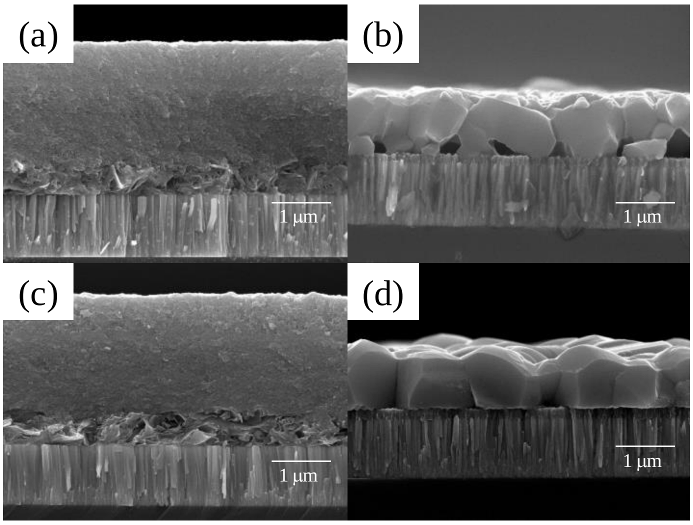

Fig. 1. Cross-sectional SEM images of the as-prepared CZTS thin films on (a) as-coated and (c) annealed SnS buffer layers. SEM of surfurized CZTS thin films on (b) as-coated and (d) annealed SnS buffer layers.

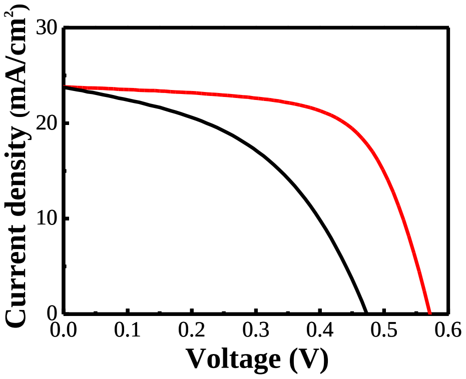

Fig. 2. I–V characteristic of the CZTS solar cells using as-coated (solid) and annealed SnS (dotted) buffer layers.

Table 1 Summary of element ratio and cell parameters of CZTS solar cells prepared on as-coated and annealed SnS interlayers.

SnS	Cu/Zn+Sn	Zn/Sn	Efficiency %	FF %	V_{oc} (mV)	J_{sc} (mA/cm^2)	R_s (Ω cm^2)	R_p (Ω cm^2)
As-coated	0.87	1.07	5.1	45	470	24.2	50	581
Annealed	0.86	1.06	8.8	64	570	24.1	24	2226

Fig. 2 illustrates the current–voltage (I–V) characteristics of the CZTS solar cells with different SnS buffer layers. Table 1 lists the parameters of the CZTS solar cells. The efficiency of the CZTS solar cell with the as-coated SnS buffer layer was 5.1%, and it increased to 8.8% when the annealed SnS buffer layer was used. For the CZTS solar cell using the as-coated SnS interlay, the open-circuit voltage (V_{oc}) was 470 mV, short-circuit current (J_{sc}) was 24.2 mA/cm^2, and fill factor was 45%. The low V_{oc} and fill factor were due to the voids at the CZTS–MoS$_2$ interface that could cause a recombination of holes. For the CZTS solar cell with the annealed SnS buffer layer, the voids were considerably reduced and the parameters were much improved. The J_{sc} was 24.1 mA/cm^2, V_{oc} was 570 mV, and fill factor was 64%.

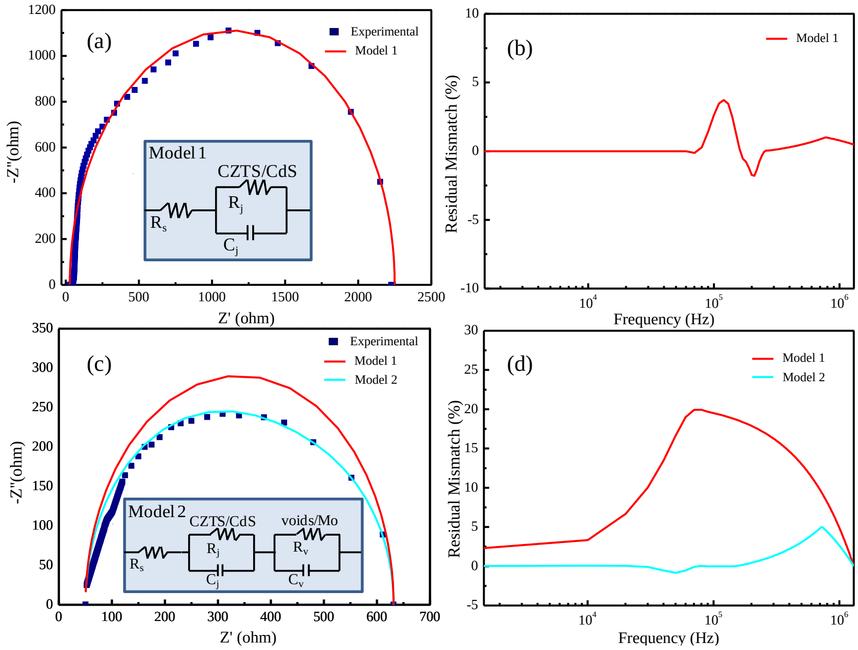

Fig. 3. Impedance spectra of CZTS solar cells prepared by (a) annealed SnS buffer layer and (c) as-coated SnS buffer layer; (b) and (d) show the deviation between the simulated and measured spectra for (a) and (c), respectively.

Fig. 3 shows the complex impedance as a function of the frequency. The Nyquist plots of the CZTS solar cells fabricated using the annealed and as-coated SnS buffer layers are presented in Fig. 3(a) and (c), respectively. The impedance spectra were measured in the dark under the zero reverse bias condition. Two equivalent-circuit models are proposed in the insets, and the corresponding curve fittings are shown by solid lines in Fig. 3(a) and (c). Model 1 corresponds to an equivalent circuit consisting of a resistance (R_s) in parallel with a capacitance (C_j) and connected to a series resistance R_s. Model 2 presents two parallel R–C circuits in series and connected to a series resistance.

The fitting mismatch between the simulated and measured data of Fig. 3(a) and (c) are shown in Fig. 3(b) and (d), respectively. Model 1 shows satisfactory fitting results with a deviation smaller than 5% for the CZTS with the annealed SnS buffer layer for all frequency regions. The extracted R_s, R_j, and C_j values were 24 Ω.cm^2, 2226 Ω.cm^2, and 55 nF.cm^{-2}, respectively. However, the CZTS device that had voids at the interface cannot be modeled simply by one R/C model. An additional R_v/C_v circuit was required to account for the voids at the Mo–CZTS interface, as indicated in Model 2. The second resistance–capacitance loop modified the fitting curve and reduced the mismatch between the simulation and measurement. The deviation decreased from 20% (Model 1) to 5% (Model 2). The extracted R_s, R_j, C_j, R_v, and C_v values were 50 Ω.cm^2, 460 Ω.cm^2, 49 nF.cm^{-2}, 119 Ω.cm^2, and 41 nF.cm^{-2}, respectively.

4. Conclusions

This study examined the effects of SnS buffer layers on the photovoltaic properties of solution-prepared CZTS devices. The annealed SnS layer improved the CZTS quality by eliminating the voids at the CZTS–MoS_2 interface. By contrast, the CZTS prepared on the as-coated SnS had many interfacial voids. An additional capacitance–resistance circuit in parallel that was responsible for the interfacial defects was required to fit the admittance spectrum of the CZTZ prepared on the as-coated SnS.

The efficiency of the CZTS solar cell prepared on the annealed SnS was 8.8%, open-circuit voltage was 570 mV, short-circuit current was 24.1 mA/cm^2, and fill factor was 64%. The open-circuit voltage and fill factor increased to 43% and 72%, respectively, when the buffer layer changed from the as-coated SnS to the annealed SnS.

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