

RESEARCH ARTICLE

Co-optimization of SnS absorber and Zn(O,S) buffer materials for improved solar cells

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ABSTRACT

Thin-film solar cells consisting of earth-abundant and non-toxic materials were made from pulsed chemical vapor deposition (pulsed-CVD) of SnS as the *p*-type absorber layer and atomic layer deposition (ALD) of Zn(O,S) as the *n*-type buffer layer. The effects of deposition temperature and annealing conditions of the SnS absorber layer were studied for solar cells with a structure of Mo/SnS/Zn(O,S)/ZnO/ITO. Solar cells were further optimized by varying the stoichiometry of Zn(O,S) and the annealing conditions of SnS. Post-deposition annealing in pure hydrogen sulfide improved crystallinity and increased the carrier mobility by one order of magnitude, and a power conversion efficiency up to 2.9% was achieved. Copyright © 2014 John Wiley & Sons, Ltd.

KEYWORDS

SnS thin-film solar cell; zinc oxysulfide; buffer layer; atomic layer deposition; pulsed-chemical vapor deposition

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1. INTRODUCTION

Tin monosulfide (SnS) has shown to be a promising alternative *p*-type absorber material to conventional Cu(In,Ga)(S,Se)₂ (CIGS) and CdTe due to its earth abundancy and non-toxicity, suitable bandgap of 1.1–1.5 eV [1,2], and high absorption coefficient above 10⁴ cm⁻¹ [3,4]. Furthermore, SnS is a binary compound that involves simpler growth chemistry compared to Cu₂ZnSn(Se,S)₄ [5,6], another investigated earth-abundant absorber material. Zinc oxysulfide, Zn(O,S), has shown to be a promising non-toxic *n*-type buffer layer to replace the conventional toxic CdS [7,8] in CIGS-based solar cells [8]. Zn(O,S) allows simple tuning of the conduction band offset (CBO) at the *p*-*n* junction interface by optimizing the oxygen and sulfur contents of Zn(O,S) [9–11], which can be easily done with atomic layer deposition (ALD) by altering the number of pulses for each precursor [7,12,13]. Such tunability of the buffer layer is important, since a “cliff” structure in the conduction-band energy alignment ($E_{c,absorber} > E_{c,buffer}$) increases interface recombination, whereas a “spike” structure ($E_{c,absorber} < E_{c,buffer}$) forms a barrier that blocks

photocurrent collection for CBO larger than 0.5 eV [8,14–19]. Recently, heterojunction solar cells using a *p*-type SnS absorber layer and an *n*-type ZnO-based buffer layer have shown to be a promising path towards earth-abundant non-toxic thin-film solar cells exhibiting a certified total-area record efficiency of 2.04% (uncertified active-area efficiency of 2.46%) with Zn(O,S) buffer layers [9], and an efficiency of 2.1% with Zn_{1-x}Mg_xO buffer layers [20]. Although SnS exhibits properties suitable for an absorber layer, grain boundaries and defects such as sulfur vacancies in the bulk can induce recombination centers, which diminish the performance of the solar cells [21]. Such defects can be reduced or eliminated by providing sulfur to the film through an appropriate post-annealing atmosphere.

In this paper, we grow SnS by pulsed-chemical vapor deposition (pulsed-CVD) from a cyclic tin(II) amide precursor [22] and improve its quality by varying the temperatures of growth and post-deposition annealing. The device performance was further improved by optimizing the oxygen and sulfur contents of the Zn(O,S) buffer layer. Since different growth and annealing conditions of SnS

can change the conduction-band energy level of the absorber layer, tuning of the CBO through the Zn(O,S) buffer layer composition is critical to optimizing the band alignment across the junction [23]. For the optimum conditions, the solar cell efficiency reaches 2.9%, the highest yet reported for solar cells with SnS as the absorber layer.

2. EXPERIMENTAL PROCEDURE

Solar cell devices with a structure of Si/SiO₂/Mo/SnS/Zn(O,S)/ZnO/ITO/Ag were fabricated. A schematic diagram of the device stack is shown in Figure 1(a). A bilayer of Mo (1 μm, 0.3 ohm/sq) was sputtered onto silicon (100) substrates with about 300 nm of silicon dioxide on top. The first layer of Mo was sputtered for 30 min at a working pressure of 10 mTorr, and the second layer for 30 min at 2 mTorr [24].

A pulsed-CVD process was used to grow ~500 nm of SnS using *N*²,*N*³-di-*tert*-butyl-butane-2,3-diamido-tin(II) (C₁₂H₂₆N₂Sn, Sigma Aldrich) and 4% H₂S in N₂ for the Sn and S precursors, respectively. The structure of the Sn precursor is shown in Figure 1(b). SnS films were grown at either 70°C or 120°C, and the Sn precursor source was kept at 40°C. Each pulsed-CVD cycle consisted of a dose of the Sn precursor with N₂ assistance for 1 s, then a dose of H₂S to mix and react with the Sn precursor in the deposition zone for 1 s in closed valve mode, and then evacuation for 2 s. The pressures for the Sn precursor, N₂ assist, and H₂S were 3.7, 152.4, and 154.5 Torr, respectively. The volumes of the vapor space used for dosing each precursor were approximately 13.6, 29.9, and 10.7 mL for the Sn precursor, N₂ assist, and H₂S, respectively and were all kept at 40°C. Based on these values, the exposure of each dose of Sn precursor, N₂ assist, and H₂S was approximately 0.20, 18, and 6.50 Torr·s, respectively. SnS films were annealed in pure H₂S (constant flow) with a vapor pressure of ~6.5 Torr for 1.5 h at temperatures of 200°C, 300°C, and 400°C. Based on the phase diagram of SnS

and previous studies [25,26], SnS is known to evaporate congruently, and stoichiometry of the films should remain the same for the annealing temperatures investigated in this study.

Zn(O,S) (30 nm) and ZnO (10 nm) were grown at 120°C by ALD. Diethylzinc (DEZ, Zn(C₂H₅)₂, Strem Chemicals), deionized H₂O, and a gas mixture of 4% H₂S in N₂ were used as the zinc, oxygen, and sulfur sources at room temperature, respectively. The pressures for the Zn precursor, H₂O, and H₂S were 7.5, 7.8, and 154.5 Torr, respectively. The exposures used for each dose of DEZ, H₂O, and H₂S are estimated to be approximately 0.13, 0.15, and 6.50 Torr·s with trapped volumes of 4.4, 4.8, and 10.7 mL, respectively, which were all kept at 40°C. Each precursor was exposed to the substrate for 1 s using closed valve mode. The purge times for each precursor were 30, 30, and 10 s for DEZ, H₂O, and H₂S, respectively. The ALD sequence for Zn(O,S) was (DEZ/N₂/H₂O/N₂) × *m* + (DEZ/N₂/H₂S/N₂) × *n*, where *m* and *n* indicate the number of pulses for ZnO and ZnS, respectively.

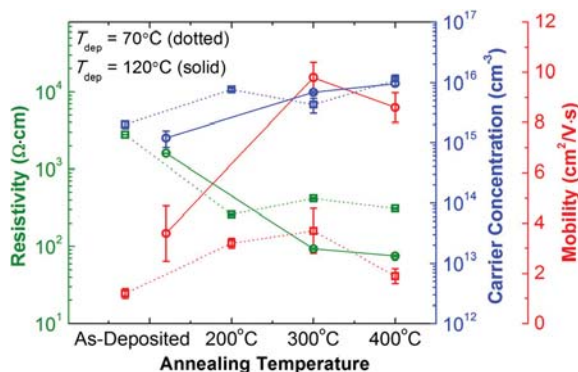


Figure 2. (Color) Plot of resistivity (green), hole carrier concentration (blue), and hole mobility (red) vs. annealing temperature in H₂S, for SnS films deposited at 70°C (dotted) and 120°C (solid). Resistivity and carrier concentration are plotted on a semilog scale, whereas mobility is plotted on a linear scale.

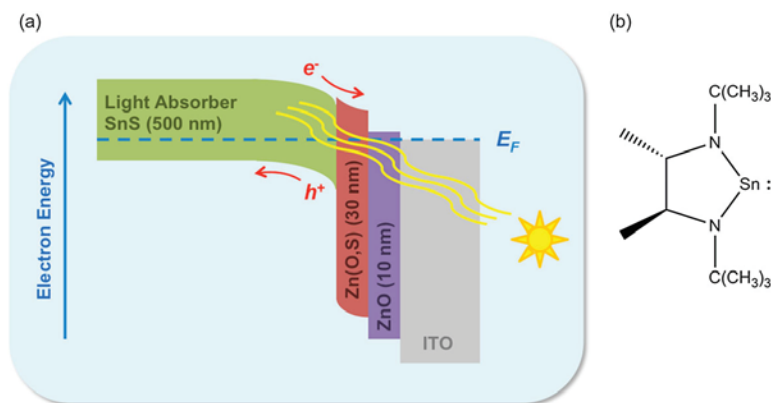


Figure 1. (Color) (a) Schematic diagram of the solar-cell device stack under short-circuit conditions and (b) structural formula for the Sn precursor. SnS/Zn(O,S) band-alignment was drawn in accordance with the ultraviolet photoelectron spectroscopy (UPS) measurements from previous study by L. Sun *et al.* [23].

Stoichiometry of the Zn(O,S) films was measured by Rutherford backscattering spectroscopy (RBS). By RF magnetron sputtering, 200 nm of indium tin oxide (ITO) was deposited at room temperature through a shadow mask to define the device area (0.25 cm^2). For the top electrode, 500 nm of Ag was electron-beam evaporated through a shadow mask at room temperature.

Current density vs. voltage (J - V) characteristics were measured with a Keithley 4200 sourcemeter. The standard 100 mW/cm^2 (1 Sun) illumination was generated by a Newport Oriel 91194 solar simulator with a 1300-W Xe-lamp using an AM1.5G filter, and a Newport Oriel

68951 flux controller calibrated by an NREL-certified Si reference cell equipped with a BK-7 window. External quantum efficiency (EQE) measurements were performed with a PV Measurements Model QEX7 tool at room temperature.

Van der Pauw measurements of the Hall effect were used to determine the carrier concentration and carrier type of individual layers. The carrier mobility was then determined from $\rho = 1/pe\mu$, where ρ is the resistivity, p is the carrier concentration, e is the electron charge, and μ is the carrier mobility. Cross-sectional (with 12° tilt) and plan-view morphology of SnS films were examined by field-emission

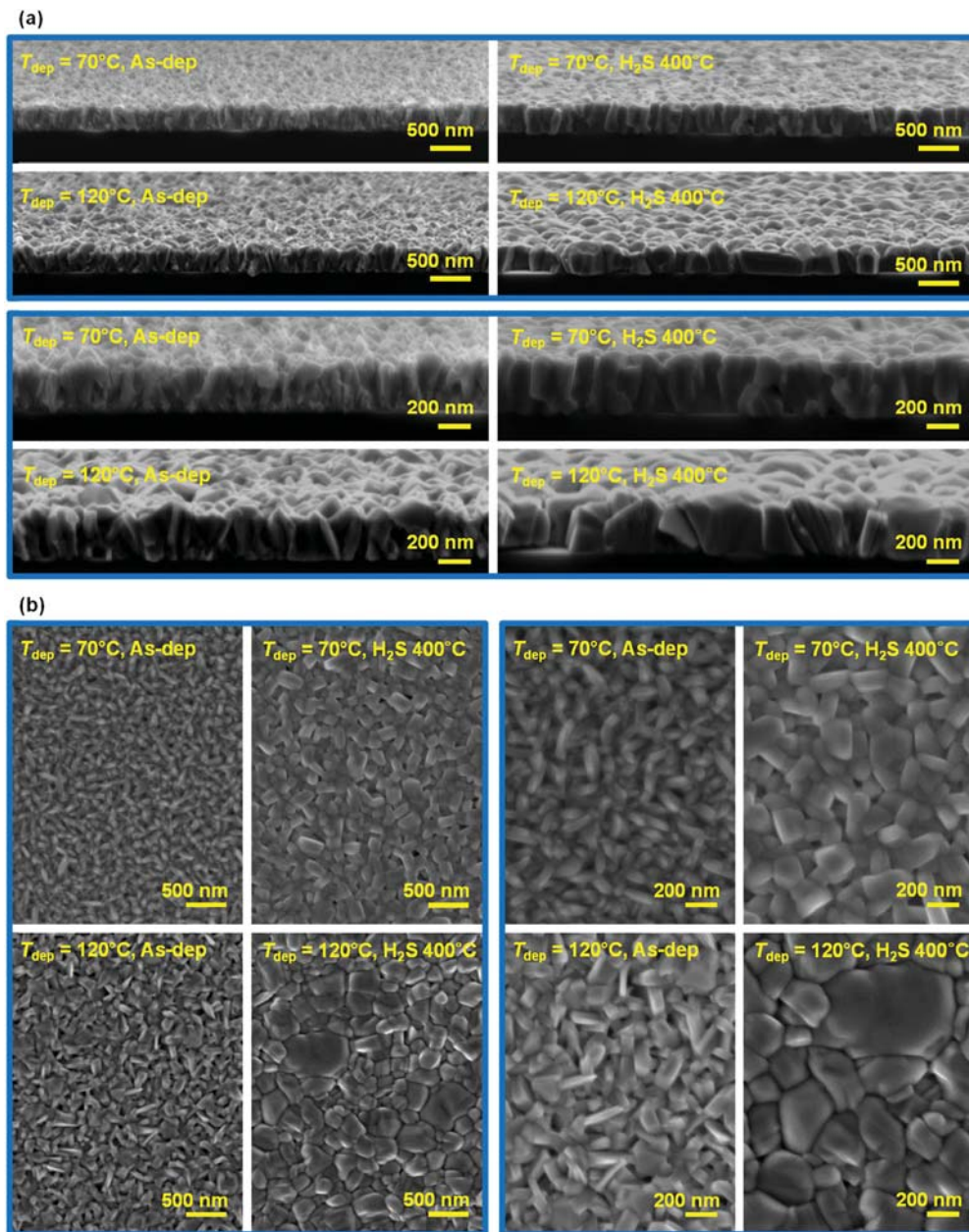


Figure 3. (Color) (a) Cross-sectional (with 12° tilt) and (b) plan-view FESEM images of as-deposited SnS grown at 70°C and 120°C , and SnS post-annealed at 400°C in H_2S .

scanning electron microscopy (FESEM, Zeiss, Ultra-55). The crystal structure and texture of the films were analyzed by X-ray diffraction (XRD, PANalytical X-Pert Pro) with Cu $K\alpha$ radiation using a θ - 2θ scan. SnS films were grown on quartz substrates for Hall measurements, on a layered substrate of Si/SiO₂/Mo for XRD analysis, on glassy carbon substrates for RBS, and on Si(100) substrates for FESEM.

3. RESULTS AND DISCUSSION

The dependence of H₂S annealing temperature on the electrical properties of SnS were investigated. Figure 2 compares SnS films grown at 70°C (dotted) and 120°C (solid). Resistivity of the films tended to decrease with increasing annealing temperature, and hole carrier concentrations ranged from 10¹⁵ to 10¹⁶ cm⁻³ for both deposition temperatures. The hole mobility increased with the H₂S annealing temperatures due to the decrease in resistivity. Raising the deposition temperature from 70°C to 120°C improved the mobility of the as-deposited SnS film from 1 to 4 cm²/V·s. The mobility of the as-deposited film grown at 120°C is comparable to the film grown at 70°C and annealed at 300°C. Annealing films grown at 120°C, improved the mobility from 4 to 10 cm²/V·s. The enhanced mobility could be due to the improvement of crystallinity (point and extended defects). Grain growth from annealing is observed in the cross-sectional and plan-view SEM images shown in Figure 3. Much larger grain growth after H₂S annealing was observed for the higher deposition temperature. This is because the grains of the as-deposited film grown at 120°C start off larger than those grown at 70°C. Raising the deposition temperature to 120°C also eliminated pinholes that were observed to increase in number with annealing temperature for films deposited at 70°C.

For SnS films grown at 120°C, the effect of H₂S annealing temperature on the solar-cell performance was investigated for a fixed Zn(O,S) buffer layer with S/Zn = 0.37, as determined by RBS. Figure 4 shows J - V plots under dark and 1 Sun illumination. Compared to the device

with as-deposited SnS, the devices with SnS annealed in pure H₂S resulted in larger short-circuit current densities (J_{SC}) and open-circuit voltages (V_{OC}) due to the improvement of the SnS absorber layer quality. The improvement in V_{OC} can be explained by the overall tendency shown in the dark saturation current, whereas the improvement in J_{SC} can be explained by the improved carrier collection (Figure 7a). The device with SnS annealed at 300°C showed a cell performance of $J_{SC} = 17.9$ mA/cm², $V_{OC} = 256$ mV, $FF = 42.0\%$, and $\eta = 1.9\%$, and the device with SnS annealed at 400°C showed a cell performance of $J_{SC} = 18.5$ mA/cm², $V_{OC} = 235$ mV, $FF = 42.8\%$, and $\eta = 1.9\%$, as summarized in Table I. The device with SnS annealed at 300°C showed improvement with less leakage current compared to the device with as-deposited SnS. However, the leakage current increased when annealing SnS at 400°C in pure H₂S, resulting in lower V_{OC} .

For devices with SnS annealed in H₂S at 300°C and 400°C, different stoichiometries of Zn(O,S) were investigated to further improve the band alignment of the solar cell, as shown in the J - V characteristics under dark and 1 Sun illumination in Figure 5. For both SnS annealing temperatures, higher sulfur content in Zn(O,S) led to lower current leakage. For the devices with SnS annealed at 300°C, as the sulfur content in Zn(O,S) increased, the J_{SC} decreased, and the V_{OC} increased due to the increase in the conduction band energy level of Zn(O,S) [23]. For Zn(O,S) with S/Zn = 0.50, the device performance improved with $J_{SC} = 14.1$ mA/cm², $V_{OC} = 305$ mV, and $FF = 53.1\%$, as summarized in Table II. The efficiency increased to

Table I. Solar cell parameters of devices with Zn(O,S), S/Zn = 0.37 as the buffer layer.

SnS annealing	J_{SC} (mA/cm ²)	V_{OC} (mV)	FF (%)	η (%)
As-deposited, $T_{dep} = 120^\circ\text{C}$	7.8	200	36.2	0.6
H ₂ S 200°C	14.4	222	45.7	1.5
H ₂ S 300°C	17.9	256	42.0	1.9
H ₂ S 400°C	18.5	235	42.8	1.9

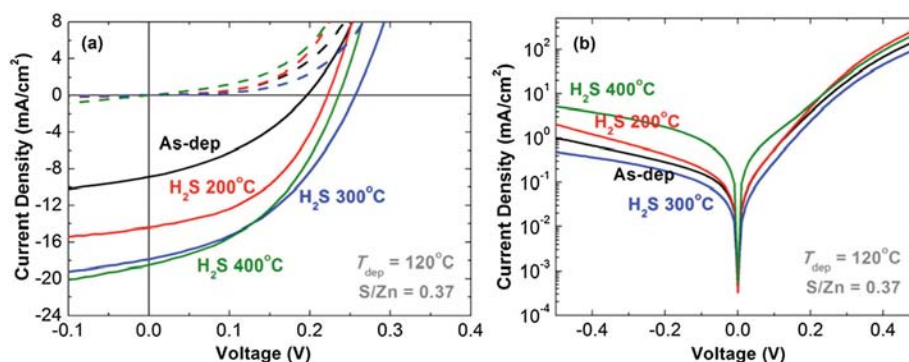


Figure 4. (Color) (a) Current density vs. voltage (J - V) plots under dark (dotted) and 1 Sun illumination (solid) and (b) semilog J - V plots under dark for devices with the SnS layer annealed at different temperatures having Zn(O,S), S/Zn = 0.37 as the buffer layer.

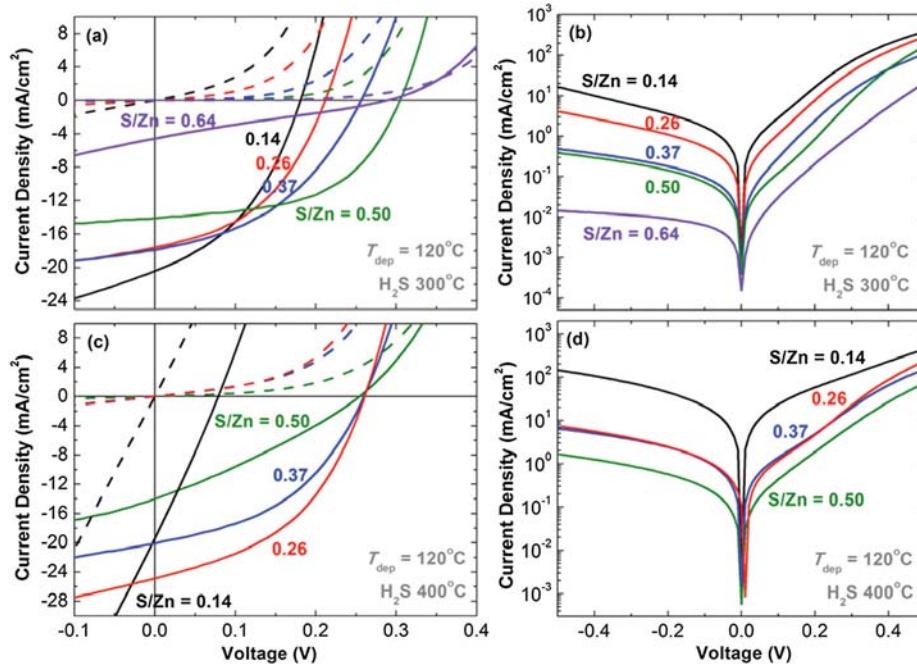


Figure 5. (Color) (a, c) J - V characteristics under dark (dotted) and 1 Sun illumination (solid) and (b, d) semilog J - V characteristics under dark for devices with varied stoichiometry of the Zn(O,S) buffer layer. Comparison of the SnS layer annealed in H_2S at 300°C (a, b) and 400°C (c, d).

Table II. Comparison of solar cell parameters of devices with SnS deposited at 120°C and annealed at 300°C and 400°C using different Zn(O,S) layers.

SnS annealing	S/Zn in Zn(O,S)	J_{SC} (mA/cm ²)	V_{OC} (mV)	FF (%)	η (%)
H ₂ S 300°C	0.14	20.4	181	40.1	1.5
	0.26	17.6	212	43.7	1.6
	0.37	17.9	256	42.0	1.9
	0.50	14.1	305	53.1	2.3
	0.64	4.6	289	25.1	0.3
H ₂ S 400°C	0.14	19.4	79	26.4	0.4
	0.26	24.9	261	44.4	2.9
	0.37	20.1	260	43.9	2.3
	0.50	14.0	254	29.3	1.1

$\eta = 2.3\%$, due to the improvement in V_{OC} and FF . However, for Zn(O,S) with $S/Zn > 0.50$, the device performance significantly deteriorated because the conduction band energy level of Zn(O,S) was too high, impeding the photo-generated electron flow, and resulting in very low J_{SC} and poor FF . For the devices with SnS annealed at 400°C and Zn(O,S) with $S/Zn = 0.14$, the rectifying behavior was lost due to the high conductivity of the buffer layer. For the devices with SnS annealed at 400°C and Zn(O,S) with $S/Zn > 0.14$, the J_{SC} increased with decreasing sulfur content in the buffer layer. The solar cell performance improved to $J_{SC} = 24.9 \text{ mA/cm}^2$, $V_{OC} = 261 \text{ mV}$, $FF = 44.4\%$, and $\eta = 2.9\%$ for Zn(O,S) with $S/Zn = 0.26$ and SnS

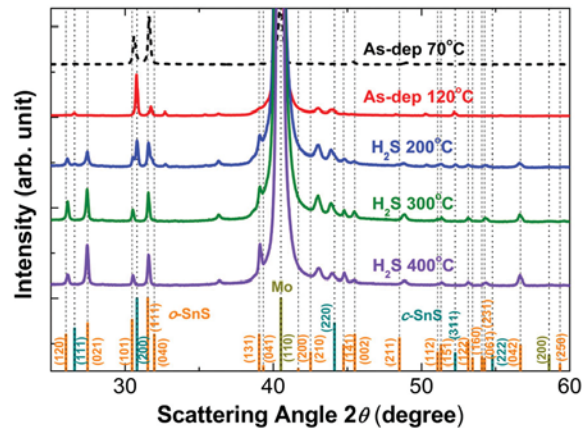


Figure 6. (Color) X-ray diffraction scans of the as-deposited SnS grown at 70°C and 120°C, and SnS films grown at 120°C annealed in pure H_2S at various temperatures. Vertical lines represent orthorhombic SnS (o -SnS), cubic SnS (c -SnS), and Mo diffraction peak positions listed by JCPDS Nos. 00-039-0354, 04-004-8426, and 00-004-0809, respectively.

annealed at 400°C. For the devices with SnS annealed at 300°C and 400°C, the optimum Zn(O,S) S/Zn ratios were 0.50 and 0.26, respectively. This variation in optimum Zn(O,S) sulfur content is probably due to the change in surface conduction-band position of SnS from the different annealing conditions, leading to different CBO at the SnS/Zn(O,S) interface.

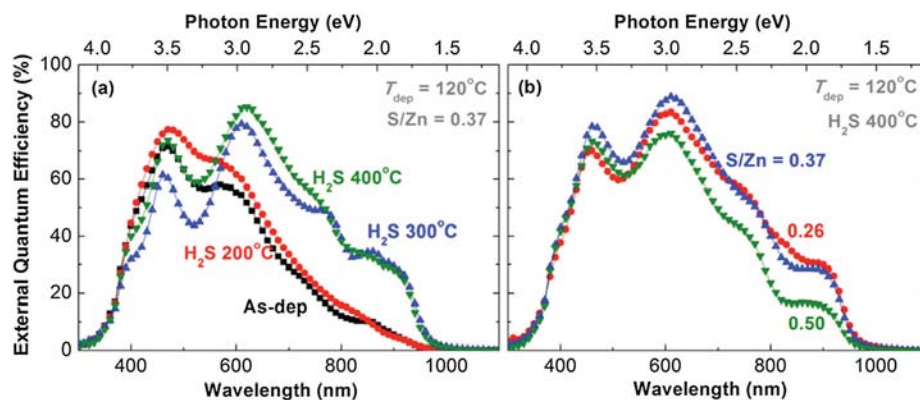


Figure 7. (Color) External quantum efficiency (EQE) of the various solar cell devices.

Figure 6 shows the XRD scans of as-deposited SnS grown at 70°C, and as-deposited and H₂S annealed SnS films grown at 120°C. The as-deposited films mainly have the cubic structure (JCPDS No. 04-004-8426) that is reported to be stable at low temperatures [27]. After annealing, the films convert to the orthorhombic phase (JCPDS No. 00-039-0354) that is stable at higher temperatures [28]. The orthorhombic (111) peak of SnS decreases as the deposition temperature increases from 70°C to 120°C. For films grown at 120°C, the orthorhombic (111) peak increases with H₂S annealing, and the orthorhombic (021) peak increases with increasing annealing temperature. Such change in crystal orientation from the different annealing temperatures is probably why the surface conduction-band position of SnS changes [29–31], resulting in variation of the optimum Zn(O,S) sulfur content for the solar cell devices [9].

EQE measurements can be found in Figure 7. For devices with increasing annealing temperature of SnS, EQE near the high wavelength region ($\lambda > 600$ nm) increased significantly, whereas EQE near the low wavelength region ($\lambda < 450$ nm) remained approximately the same. The EQE enhancement at high wavelengths indicates collection-length improvement with H₂S annealing of SnS. Crystallinity improvement could be a possible reason for the improvement in collection length as shown by the increased red light response. For devices with SnS annealed at 400°C, EQE remained similar in the low wavelength region ($\lambda < 450$ nm) despite the different sulfur contents in Zn(O,S), which is probably because Zn(O,S) is only 30 nm thick, allowing the ITO layer to do most of the absorbing for the low-wavelength region. The overall EQE increased with decreasing sulfur content in Zn(O,S), which agrees well with the J - V characteristics under illumination.

4. CONCLUSIONS

Devices with efficiencies up to 2.9% were achieved through improvement of the SnS absorber layer quality via annealing and varying the stoichiometry of Zn(O,S). We successfully demonstrated solar-cell device improvements through

annealing the SnS absorber layer in pure H₂S, which improves crystallinity and reduces the density of grain boundaries. Different deposition and annealing temperatures can lead to variations of the surface conduction-band positions of SnS, which is why it is beneficial to use a buffer layer with variable compositions like Zn(O,S) so that the CBO at the p - n junction interface can be easily optimized.

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