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# Chemically Deposited CdS Buffer/Kesterite Cu<sub>2</sub>ZnSnS<sub>4</sub> Solar Cells: Relationship between CdS Thickness and Device Performance

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**Supporting Information** 

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**ABSTRACT:** Earth-abundant, copper-zinc-tin-sulfide (CZTS), kesterite, is an attractive absorber material for thin-film solar cells (TFSCs). However, the open-circuit voltage deficit ( $V_{oc}$ -deficit) resulting from a high recombination rate at the buffer/ absorber interface is one of the major challenges that must be overcome to improve the performance of kesterite-based TFSCs. In this paper, we demonstrate the relationship between device parameters and performances for chemically deposited CdS buffer/CZTS-based heterojunction TFSCs as a function of buffer layer thickness, which could change the CdS/CZTS interface conditions such as conduction band or valence band offsets, to gain deeper insight and understanding about the  $V_{oc}$ -deficit behavior from a high recombination rate at the CdS buffer/kesterite interface. Experimental results show that device parameters and performances are strongly dependent on the CdS buffer thickness. We postulate two meaningful consequences: (i) Device parameters were improved up to a CdS buffer thickness of 70 nm, whereas they deteriorated at a thicker CdS buffer layer. The  $V_{oc}$ -deficit in the solar cells improved up to a CdS buffer thickness of 92 nm and then deteriorated at a thicker CdS buffer layer. (ii) The minimum values of the device parameters were obtained at 70 nm CdS thickness in the CZTS TFSCs. Finally, the highest conversion efficiency of 8.77% ( $V_{oc}$ : 494 mV,  $J_{sc}$ : 34.54 mA/cm<sup>2</sup>, and FF: 51%) is obtained by applying a 70 nm thick CdS buffer to the Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> absorber layer.

KEYWORDS: earth-abundant elements, copper-zinc-tin-sulfide (CZTS), thin-film solar cells, CdS buffer, device performance

# INTRODUCTION

Kesterite, copper-zinc-tin-sulfoselenide, and its related compounds, Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS), Cu<sub>2</sub>ZnSnSe<sub>4</sub> (CZTSe), and  $Cu_2ZnSn(S_x,Se_{1-x})_4$  (CZTSSe), have recently emerged as some of the most promising materials for thin-film solar cells (TFSCs) because of their natural abundance, outstanding lightabsorbing ability, and high theoretical efficiency.<sup>1-9</sup> A record power conversion efficiency (PCE) of  $\eta = 12.6\%$  has been achieved by IBM using a CZTSSe absorber layer prepared by an approach requiring highly toxic and flammable hydrazine.<sup>1</sup> However, the achieved PCE for kesterite-based compounds is still far behind those of commercialized TFSCs such as  $Cu(In,Ga)(S,Se)_2$  (CIGS) ( $\eta = 22.6\%$ )<sup>11</sup> and CdTe ( $\eta =$ even though they possess higher theoretical 22.1%),<sup>12</sup> efficiencies (CZTS: 32.4% and CZTSe: 31.0% under singlejunction conditions).<sup>13</sup> Among the factors causing the underperformance, the open-circuit voltage deficit ( $V_{oc}$ -deficit:  $E_g/q - V_{oc}$  where  $E_g$  is the band gap energy of the kesterite and q is the electron charge) is a critical factor in kesterite-based TFSCs.<sup>5,14–21</sup> The value of  $V_{oc}$ -deficit in kesterite-based TFSCs with outstanding performance is more than 600 mV, which is slightly higher than that of the CIGSSe TFSCs (about 440 mV).<sup>19,22</sup> Several possible reasons have been proposed to explain the  $V_{oc}$ -deficit in kesterite-based TFSCs. Secondary phases usually formed during annealing in chalcogenide atmospheres, located at the absorber material surface, near the back contact, or within the kesterite layer, can hinder the charge carrier transport and lead to an increase in the

Received: June 27, 2017 Accepted: October 5, 2017 Published: October 5, 2017 recombination rate, leading to underperformance in the device.  $^{1,5,23}$  Other persuasive reasons for losses in  $V_{\rm oc}$  include band gap fluctuations because of the locally varying ionization of defects ( $\rm V_{Cu}$ ) and atomic-level antisite defects such as  $\rm Cu_{Zn'}$   $\rm Zn_{Cu'}$ ,  $\rm Cu_{Sn'}$ ,  $\rm Sn_{Cu'}$ ,  $\rm Zn_{Sn}$ , and  $\rm Sn_{Zn'}$ , resulting from the nonuniformities in the crystal structure or the compositional ratio of the kesterite.  $^{4,14,15,18-21,24-28}$  Specifically, multioxygen state elements such as Cu and Sn in CZTS commonly generate deep defects that increase the nonradiative carrier recombination and thus significantly affect the  $V_{\rm oc}.^{23}$ 

Another possible reason for  $V_{oc}$ -deficit is the high recombination rate at the buffer/kesterite interface, resulting from the mismatched band alignment between CdS and kesterite layers.<sup>19</sup> Several values of conduction band offset (CBO) have been reported for CdS/kesterite heterojunction devices by various measurement techniques under different interface conditions.<sup>29,30</sup> On the basis of first-principles calculations, the value of CBO is negative, a so-called "clifflike" CdS/kesterite heterojunction.<sup>29</sup> It has been suggested that the cliff-like CBO leads to the high interface recombination rate and thereby  $V_{0c}$ -deficit behavior. The cliff-like band alignment between the CdS/kesterite layers acts as a barrier to injected electrons (majority carriers) from the CdS buffer to the kesterite absorber under forward bias.<sup>30–33</sup> The electrons lead to the interface recombination current between the holes in kesterite and electrons at the CdS/kesterite interface. This electrical behavior impacts the reduction of  $V_{\rm oc}$  under wide band gap conditions in the sulfide-rich kesterite absorber.<sup>14</sup> On the other hand, many reports have proposed that the optimal band alignment of the CdS/kesterite interface, a so-called "spike-like" type (positive offset), is more favorable than that of the cliff-like type because it can reduce the CdS/kesterite interface recombination of majority carriers, which prevents the reduction of  $V_{oc}$ .<sup>19,30,32,33</sup> Some researchers have proposed the following to solve this problem: (i) alkali elements such as Na and K or Ge in the kesterite compounds during synthesis to enhance the growth of grains to large size as well as to reduce antisite defects in the kesterite layer<sup>9,24,25,27,34–38</sup> and (ii) buffer layers such as Zn<sub>1-x</sub>Cd<sub>x</sub>S, (Zn,Mg)O, Zn(O,S), and In<sub>2</sub>S<sub>3</sub> compounds to achieve the spike-like type band alignment.<sup>33,39–42</sup>

Although the introduction of additive elements in the kesterite and alternatives to CdS in the buffer layers has been suggested as a promising possibility for the improvement of performance, improvements over kesterite-based TFSCs with CdS buffer have not been realized. On the basis of literature surveys and to our best knowledge, there are a few research papers on the effect of chemical-bath-deposited CdS buffer thickness on the performances of kesterite-based solar cells with efficiencies below 3%.43,44 On the other hand, a few research papers reported the effect of sputtered CdS buffer thickness on the performances of CZTS-based TFSCs from 4.0 to 7.1% efficiencies.<sup>45,46</sup> Furthermore, Winkler et al. reported the improved performance of CZTSSe TFSCs, prepared by a hydrazine-based process, more than 11% through the precise optical designs such as transparent conducting oxide (TCO) and buffer layers.<sup>47</sup> Even though the solar cell device parameter analysis regarding the relationship with the device performance as a function of buffer thickness is desirable to deeply understand the loss of  $V_{oc}$  resulting from a high recombination rate at the CdS/kesterite interface, above research studies only reported the performances of the kesterite. The relationship between the buffer thickness and device performances is not

clear yet. In particular, the various thicknesses of CdS buffer layers may change the CdS/CZTS interface conditions such as CBO values because of the quantum size effect in CdS without introducing an additive element in the absorber layer and alternative buffer materials.<sup>48</sup>

In this paper, we report the preparation of the CZTS thin film prepared by annealing the sputtering-deposited metallic precursor in the chalcogenide atmospheres and chemically deposited CdS buffer and fabrication of CdS/CZTS TFSCs as a function of CdS buffer thickness. We systematically demonstrate the deeper insight and understanding on  $V_{\rm oc}$ -deficit behavior resulting from the recombination rate at the buffer/ absorber interface through the study on the relationship between device performances and parameters of CZTS-based TFSCs. Finally, an efficiency of 8.77% in the CZTSSe TFSC was achieved by applying a 70 nm thick CdS buffer to the CZTSSe absorber.

#### EXPERIMENTAL PROCEDURES

Preparation of the Metallic Precursor Thin Films. A 1  $\mu$ m thick Mo thin film was prepared by the direct current (dc) magnetron sputtering technique at room temperature on a soda-lime glass (SLG) substrate. The substrates were cleaned ultrasonically using acetone, methanol, isopropyl alcohol, and deionized (DI) water for 10 min consecutively. The metallic precursor stacked with Cu/Sn/Zn was prepared on Mo-coated SLG substrates (0.5  $\Omega/sq$ , sheet resistance) using the dc magnetron sputtering technique. The Mo-coated SLG substrates were placed in the sputtering chamber under  $1.0 \times 10^{-6}$ Torr. Each metallic target used had a 99.999% purity (TASCO, Korea). The sputtering conditions of each metallic layer were as follows: Cu (0.68 W/cm<sup>2</sup>, 8 mTorr, 2600 s), Sn (0.68 W/cm<sup>2</sup>, 8 mTorr, 1852 s), and Zn (0.68 W/cm<sup>2</sup>, 8 mTorr, 1525 s). The substrates were rotated at 5 rpm during the sputtering process. The Mo-coated SLG substrates were cooled using a custom cooling chuck. To improve the morphologies and microstructures of the as-deposited Zn and Sn layers, the growth rate was controlled by maintaining the substrate temperature at 0 °C. The metallic precursor thin films were then soft-annealed at 300  $^\circ C$  for 10 min under an  $N_2$  atmosphere to improve their morphology. Detailed information on Experimental Procedures can be found elsewhere.<sup>13</sup> The composition of the metallic precursor was Cu-poor and Zn-rich (Cu/(Zn + Sn) = 0.61, Zn/Sn =2.17), as measured by X-ray fluorescence (XRF).

Formation of CZTS and CZTSSe Thin Films by a Rapid Thermal Annealing Process. Metallic precursor thin films were individually annealed to synthesize CZTS and CZTSSe absorber thin films in an Ar + chalcogenide vapor atmosphere. Chalcogenide powders including S or S + Se were purchased from Sigma-Aldrich (with 99.999% purity), and the soft annealed metallic precursor thin films were placed into a rapid thermal annealing system. Details can be found in ref 13. The heating rate was 10 °C/s. The CZTS thin films were prepared by sulfurization at 580 °C for 10 min under 20 Torr (amount of S: 3 mg), whereas the CZTSSe thin films were prepared by sulfo-selenization at 520 °C for 10 min under 50 Torr (amounts of S and Se: 3 and 3 mg). After the annealing process, the annealed thin films were cooled at ambient temperature for 1 h. The compositional ratios of annealed thin films are Cu/(Zn + Sn) = 0.65 and Zn/Sn =1.23 (CZTS) and Cu/(Zn + Sn) = 0.57, Zn/Sn = 1.6, and Se/(S + Se) = 0.81 (CZTSSe), as measured by XRF.

**Deposition of CdS Buffer on Kesterite Films and Glass Substrates.** Before CdS buffer deposition, each of the CZTS and CZTSSe thin films was soaked in DI water for 300 s and etched with 0.2 M potassium cyanide at room temperature for 300 s, which removes the oxide-based compounds and the  $Cu_{2-x}(S,Se)_x$  phase located at the kesterite surface. The thin films were then rinsed using DI water for 60 s. Details of the removal process can be found in ref 13. Prior to the CdS buffer deposition process, the SLG substrates were cleaned ultrasonically using acetone, methanol, isopropyl alcohol, and DI water for 10 min consecutively. Further, CdS buffer deposition



Figure 1. Surface and cross-sectional FE-SEM images of (a,c) metallic precursor prepared at 0 °C with the soft annealing process at 300 °C for 10 min and (b,d) CZTS thin film by sulfurization at 580 °C for 10 min. The metallic precursor thin film shows a dense, crack-, and void-free microstructure with a thickness of ~600 nm. The sulfurized thin films have a dense microstructure with a thickness of ~1.2  $\mu$ m and a grain size ranging from 500 nm to 1.6  $\mu$ m.

was carried out on the SLG substrates and CZTS and CZTSSe absorber layers prepared by the chemical bath deposition using a precursor solution of 0.2 M CdSO<sub>4</sub>, 0.84 M ammonia, and 1.02 M thiourea at 80 °C under different deposition times ranging from 11 to 20 min. The cleaned SLG substrate and CZTS and CZTSSe thin films were immersed vertically in the reaction bath after the etching process. The color of the precursor solution was initially transparent; it changed from transparent to yellow after 6 min, and then it appeared orange after 15 min (see Figure S2a). The color of the CdS layer on SLG and CZTS absorber substrates changed from transparent to deep yellow and from gray to violet, respectively, with increasing reaction time (see Figure S2b). After deposition, the SLG substrates and kesterite thin films were taken out of the reaction bath, rinsed with DI water, and dried in air at room temperature.

**Fabrication of Kesterite-Based Solar Cells.** The CZTS and CZTSSe TFSCs were fabricated with a multilayer structure of SLG/ Mo/kesterite/CdS/i-ZnO/AZO/Al. The highly resistive, 50 nm thick i-ZnO was deposited using the radio frequency (RF) magnetron sputtering technique at room temperature, with an RF power of 75 W and a working pressure of 1 mTorr under Ar and O<sub>2</sub> mixed plasma. The 400 nm thick AZO layers were deposited using the RF sputtering technique at room temperature, with an RF power of 150 W and a working pressure of 1 mTorr under Ar plasma. The Al top grid layer was deposited using the thermal evaporation technique. The active area of the fabricated TFSCs was 0.30 cm<sup>2</sup>.

**Characterization.** The structural properties of thin films were measured using a high-resolution X-ray diffraction (XRD, X'pert PRO, Philips, Eindhoven, the Netherlands) instrument operated at 40 kV and 100 mA and analyzed using Raman scattering spectroscopy (Jobin Yvon T6400 Raman scattering system with an Olympus microscope equipped with a 100× magnification lens and in the backscattering configuration). The excitation source was an Ar laser operating at different wavelengths of 332, 532, and 632 nm. The surface morphology of the thin films was characterized by field emission scanning electron microscopy (ZSX Primus II Rigaku Corp.). The conversion efficiency and external quantum efficiency (EQE) for CZTS and CZTSSe TFSCs were characterized by a class AAA solar simulator (WXS-15SS-L2, Wacom, Japan) satisfying the conditions of AM 1.5G, 100 mW/cm<sup>2</sup>, and 25 °C and with an incident PCE

measurement unit (PV measurement, Inc.). To characterize the device parameters including shunt conductance ( $G_{\rm sh}$ ), ideality factor (A), reverse saturation current density ( $J_{\rm o}$ ), and series resistance ( $R_{\rm s}$ ) for CZTS and CZTSSe TFSCs, the J-V behavior was determined using the one-diode model described by eq 1<sup>49-51</sup>

$$J - J_{\rm L} = J_0 \exp\left[\frac{q}{AkT}(V - R_s J)\right] + \frac{V}{G_{\rm sh}}$$
(1)

where  $J_{\rm L}$  is the photocurrent, q is the electronic charge, and k is Boltzmann's constant. Hegedus et al. have extracted the diode parameters using the model shown in eq 1.<sup>50</sup> The derivative, dV/dJ, is plotted as a function of  $(J + J_{\rm L})^{-1}$ . A linear fit to the data gives an intercept of  $R_{\rm s}$  and a slope of AkT/q as defined by eq 2

$$\frac{\mathrm{d}V}{\mathrm{d}J} = R_{\mathrm{s}} + \frac{AkT}{q} (J + J_{\mathrm{L}})^{-1} \tag{2}$$

The values of  $G_{\rm sh}$  can be determined using the plots of dJ/dV versus V. The value of  $J_0$  is estimated from the *y*-intercept in the plots of  $(J + J_{\rm sc} - GV)$  versus (V - RJ).

#### RESULTS AND DISCUSSION

Characterization of Metallic Precursor and Cu<sub>2</sub>ZnSnS<sub>4</sub> Thin Films. It is well-known that the morphologies and microstructures of Zn or Sn prepared by sputtering techniques are usually quite poor because of the low melting points of Zn and Sn. The Cu/Sn/Zn-stacked metallic precursor thin films were prepared at 0 °C during the sputtering process to improve the morphologies and microstructures of Zn and Sn. The Cu/ Sn/Zn-stacked metallic precursor thin films were annealed at 300 °C for 10 min under an N<sub>2</sub> atmosphere to form the Cu-Sn and Cu-Zn alloys. These alloys can act as a temporary chalcogenide diffusion barrier during the annealing process, which can further reduce the formation of MoS<sub>2</sub> at the interface between Mo and absorber layers and form large-sized grains in the kesterite. Additional details on the effect of substrate temperature, the soft annealing process on the morphology and microstructure of Cu-Zn-Sn metallic precursor thin films, and

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the relationship between the soft annealing temperature and the thickness of Mo-chalcogenide can be found in ref 13.

Figure 1a,c shows the surface and cross-sectional FE-SEM images of Cu/Sn/Zn/Mo-stacked metallic precursor prepared at 0 °C with soft annealing at 300 °C for 10 min. Figure 1b,d shows sulfurized thin films prepared at 580 °C for 10 min. The surface FE-SEM image of the metallic precursor thin film shows a rough morphology consisting of large-sized grains (600-1000 nm) and small-sized grains (100-200 nm). The microstructure of the metallic precursor thin film shows a dense microstructure with voids and a thickness of  $\sim 600$  nm (Figure 1c). The sulfurized thin film shows very smooth surface morphology consisting of grain sizes ranging from 500 nm to 1.6  $\mu$ m. The microstructure of the sulfurized thin film is dense and compact without any voids and with grains extending from the top to the bottom of the substrate. Additionally, the formation of a thin MoS<sub>2</sub> interfacial layer between the absorber and the Mo back contact layer is also observed. The thickness of the sulfurized thin film is approximately 1.2  $\mu$ m. The sulfurized thin film consists of large-sized grains more than 1  $\mu$ m located in the upper region and small-sized grains ranging from 400 to 600 nm located in the lower region. The large grain size positively affects the device performance because smaller grains can lead to both unfavorable hopping electron transport and a higher recombination rate for charge carriers at grain boundaries in the absorber.<sup>6,7,52–54</sup>

Figure 2 shows the (a) XRD pattern and (b) Raman spectrum of the sulfurized thin film at 580 °C for 10 min. The XRD pattern of a sulfurized thin film shows strong peaks located at 28.5°, 47.3°, and 56.1° corresponding to the (112), (204), and (312) planes, respectively, for the kesterite CZTS structure (JCPDS card no. 26-0575). Several weaker peaks located at 23.1°, 29.6°, 31.8°, 33.0°, 37.0°, 37.9°, 45°, 58.9°, and 69.2° corresponding to the (110), (103), (200), (202), (211), (105), (224), and (008) planes, respectively, of the kesterite CZTS structure (JCPDS card no. 26-0575).52 The diffraction peak located near 40° is originated from the Mo substrate. Figures 2b and S2 show Raman spectra of the sulfurized thin films using different excited lasers such as 325, 532, and 632 nm to clearly distinguish the secondary phases such as ZnS<sub>2</sub>,  $Cu_{2-x}S_{xy}$ ,  $Sn_xS_{yy}$  and  $Cu_2SnS_3$ . Each of the excitation wavelengths is particularly powerful in detecting the ZnS (325 nm),  $Cu_{2-x}S_x$  and  $Sn_xS_y$  (532 and 632 nm), and Cu<sub>2</sub>SnS<sub>3</sub> (632 nm) secondary phases. The Raman spectrum using 325 nm wavelength shows no detection of the ZnSrelated peak located at 347 cm<sup>-1</sup> shown in Figure S2.<sup>52</sup> The formation of prominent kesterite CZTS was further confirmed from the presence of the major peak located at 338  $cm^{-1}$  as well as several weak peaks located at 249, 287, 350, and 375 cm<sup>-1</sup> in the Raman spectrum using 532 nm wavelength.<sup>52</sup> No observable Raman peaks from  $Cu_{2-x}S_x$  and  $Sn_xS_y$  were detected. At 632 nm wavelength, only CZTS-related Raman peaks were detected at 287, 338, and 367 cm<sup>-1</sup>; however, the Cu<sub>2</sub>SnS<sub>3</sub>-related Raman peaks located at 265 and 305 cm<sup>-1</sup> were not observed<sup>52</sup> (Figure S2). The XRD pattern and Raman spectrum characterizations suggest that the secondary phases such as  $Cu_{2-x}S_{x}$ ,  $Sn_xS_{y}$ , ZnS, and  $Cu_2SnS_3$  are not present in the kesterite thin film. Additionally, the compositional ratios of the CZTS thin film are Cu/(Zn + Sn) = 0.65 and Zn/Sn = 1.23, as measured by XRF characterization.

Characterization of Chemically Deposited CdS Buffer on the Cu<sub>2</sub>ZnSnS<sub>4</sub> Absorber and SLG Substrates. A chemically deposited CdS buffer layer is favorable in the CIGS Research Article



**Figure 2.** (a) XRD pattern and (b) Raman spectrum for the CZTS thin film using different wavelengths by sulfurization of the metallic precursor at 580 °C for 10 min. The compositional ratios of the CZTS thin film are Cu/(Zn + Sn) = 0.65 and Zn/Sn = 1.23. Indexed diffraction pattern in (a) and spectrum in (b) are the stimulated information corresponding to the tetragonal CZTS structure. All of the peaks of the CZTS thin film are matched with stick patterns and spectrum. Additional Raman spectra for CZTS thin films are found in Figure S3 in the Supporting Information using 325 and 632 nm wavelength.

and CZTSSe multilayered structured TFSCs because of the protection provided from the following: (i) modification from chemical species in the sensitive surface of the absorber and junction regions, (ii) damage caused by the subsequent physical deposition of the TCO layer, and (iii) alteration of the interface charge during the deposition process.55-59 The chemically deposited CdS thin films are generally prepared using aqueous solutions consisting of Cd salts, thiourea, and ammonia in a hot, basic medium. A typical reaction proceeds as shown in eq  $3.^{57}$  According to previous studies on the growth of the chemically deposited CdS thin film in the reaction solution, there are three different mechanisms at work: (i) the primary adherent layer is formed by the ion-by-ion deposition of Cd<sup>2+</sup> and  $S^{2-}$  on the substrate surface (heteronucleation and growth), (ii) the less adherent and more powdery films are formed by the cluster-by-cluster mechanism through the adsorption and aggregation of CdS cluster precipitated in a bulk solution (homonucleation and growth), and (iii) a mixed mechanism where the predominance of one mechanism over another is governed by the extent of ion-by-ion and cluster-bycluster deposition.

$$Cd(NH_3)_4^{2+} + CS(NH_2)_2 + 2OH^-$$
  
 $\rightarrow CdS + CH_2N_2 + NH_3 + 2H_2O$  (3)

The key factors include the degree of supersaturation of the solution and the catalytic activity of the substrate surface.<sup>55–59</sup>



Figure 3. Representative surface and cross-sectional FE-SEM images of CdS thin films prepared on the SLG substrate (a,b) and on the Cu<sub>2</sub>ZnSnS<sub>4</sub> thin film (c,d) at 80 °C for 13 min. The morphologies and microstructures of CdS thin films are quite different on the SLG substrate and on the CZTS thin films.

Figure 3 shows the representative surface and cross-sectional FE-SEM images of CdS thin films prepared on the SLG substrate (a,c) and on the CZTS absorber (b,d) at 80 °C. The CdS thin film prepared on the SLG substrate (Figure 3a,b) exhibits a nonuniform distribution of spherical grains with different sizes ranging from 100 to 400 nm and with many empty regions. The cross-sectional FE-SEM image shows a microstructure with many voids with a thickness of approximately 150 nm. It was also observed that some large (400 nm) grains on the SLG substrate were formed via the cluster-by-cluster mechanism at long reaction times. By contrast, the chemically deposited CdS thin film deposited on the CZTS absorber layer (Figure 3c) shows very smooth, nanoscale crystalline morphology with the presence of few large grains ranging from 100 to 300 nm in size. The microstructure of CdS on the CZTS absorber layer (Figure 3d) is uniform, compact, and densely packed with small CdS grains, is pinholefree, and has a thickness of 83 nm. Figure 4 shows the variation in the CdS buffer thickness on the CZTS absorber layer as a function of reaction times at 80 °C, which were obtained from the cross-sectional FE-SEM images (see Figure S4). The thickness of the CdS buffer increases rapidly from 48 to 123 nm up to a reaction time of 17 min and then saturates. This growth behavior is attributed to the decrease in the Cd-ammonia ligand concentration during the reaction process. Similar behavior has been observed in the chemically deposited CdS and ZnS by several researchers.<sup>55–59</sup> The significantly different morphologies of CdS on the SLG substrate and CZTS absorber layer may be attributed to the different CdS growth mechanisms during the reaction process. Previous reports of chemically deposited metal sulfide thin layers on amorphous and crystallized substrates have suggested that the growth of CdS on amorphous substrates is dominated by the cluster-bycluster mechanism, whereas the growth on crystalline substrates is dominated by the ion-by-ion mechanism or by the mixed



**Figure 4.** Variation of CdS buffer thicknesses on CZTS absorber layers as a function of reaction times at 80 °C. The thicknesses of CdS buffer were obtained from the cross-sectional FE-SEM images shown in Figure S3.

mechanism because of the catalytic activity of the substrate surfaces.  $^{57-59}$ 

Solar Cell Performances as a Function of CdS Thickness.  $V_{oc}$ -deficit characteristics in kesterite-based TFSCs are affected by the mismatched band alignment at interfaces between CdS buffer and kesterite or CIGS absorber layers which leads to the high interface recombination rate.<sup>18,19,21,26,60</sup> It has been reported that the band alignment of CdS buffer/kesterite or CdS buffer/CIGS TFSCs could be altered by adjusting the thickness of the CdS buffer or by the postannealing treatment.<sup>4,48,60,61</sup>

Therefore, we selected several thicknesses of the CdS buffer, namely, 48, 62, 70, 92, and 123 nm, to study the relationship between interface conditions and device performances in the CdS buffer/CZTS heterojunction. Figure 5 shows the device performance of the CZTS TFSCs with different thicknesses of



**Figure 5.** Device performances of the CZTS TFSCs as a function of CdS buffer thickness; (a)  $V_{oct}$  (b)  $J_{scr}$  (c) FF, and (d)  $\eta$  under AM 1.5G illuminations. Each dataset was obtained from five to six solar cells.

the CdS buffer: (a) open-circuit voltage  $(V_{oc})$ , (b) short-circuit current density  $(J_{sc})$ , (c) fill factor (FF), and (d) efficiency  $(\eta)$ under AM 1.5G illumination. Each dataset was obtained from five or six solar cells. The average performance of the CZTS TFSCs improved when the CdS buffer thickness is increased up to 70 nm, whereas the average performance deteriorates with further increase in the CdS layer thickness. Surprisingly, the average values of  $J_{sc}$  and  $\eta$  of CZTS TFSCs are dramatically improved with increased thickness up to 70 nm compared to the other device parameters.

Figure 6 shows the (a) current-voltage (J-V) curve and (b) EQE of devices with the best performance as a function of CdS



**Figure 6.** (a) J-V, (b) EQE, and (c) integrated current densities from the EQE of the best performance among each solar cell as a function of CdS buffer thickness.

buffer thickness. All of the performance parameters (except  $V_{\rm oc}$ ) of the CZTS TFSCs improve with increased CdS buffer thickness up to 70 nm and then deteriorate with CdS thickness thicker than 70 nm. The CZTS solar cell with a 92 nm thick CdS buffer showed the best value of  $V_{\rm oc}$ . The CZTS TFSCs with the 70 nm thick CdS buffer showed the best performance parameters:  $\eta = 5.77\%$ ,  $V_{\rm oc} = 623$  mV, FF = 61%, and  $J_{\rm sc} = 15.23$  mA/cm<sup>2</sup> (see Table 2). The EQE of the CZTS TFSCs exceeds 70% in the visible region from 520 to 700 nm, except for the device with 42 nm thick CdS buffer. This poor EQE is related to the insufficient p–n formation at the interface between the CdS and CZTS layers.<sup>3</sup> The insufficient or thin CdS buffer may lead to shunt or leakage currents. The EQE in higher wavelength regions decreased regardless of the CdS buffer thickness. This behavior results from the low minority

Table 1. Obtained $J_{sc}$ Values from $J-V$ Curves, Integrated Current Densities from EQE Values, and Values of $J_{sc}$ -Integrated E	QE
for CZTS-Based TFSCs as a Function of Buffer Thickness <sup>a</sup>	

thickness (nm)	48	62	70	92	123	70 (CZTSSe)	
$J_{\rm sc}~({\rm mA/cm^2})$	7.46	9.14	15.23	13.53	12.76	34.54	
integrated EQE (mA/cm <sup>2</sup> )	6.57	12.58	14.47	13.49	12.09	34.60	
J <sub>sc</sub> -integrated EQE (mA/cm <sup>2</sup> )	+0.89	-3.44	+0.76	+0.04	+0.67	-0.06	
The integrated EQE values were obtained from integrated calculation in the Origin software.							

charge carrier lifetime and short carrier diffusion caused by the high defect density in the kesterite absorber layer, and it is a common problem for kesterite-based solar cells.<sup>10,62</sup>

The EQE at wavelengths ranging from 360 to 500 nm, which is attributed to the absorption in the CdS buffer, decreases with increasing thickness of CdS buffers except for the 42 nm thick CdS layer. The band gap energy of the CZTS absorber layer as estimated from the EQE graph is  $1.51 \pm 0.02$  eV (Figure S5). Figure 6c and Table 1 show integrated current densities and gap values between measured and integrated current densities from EQE graphs (Figure 6b) of the best performance among each solar cell as a function of CdS buffer thickness. It is similar values between integrated current densities from EQE graph and measured  $J_{sc}$  except for that at 62 nm. This difference between the integrated current density from EQE and  $J_{sc}$  at 62 nm may be attributed to the higher  $R_s$  and  $G_{sh}$  than those of other devices. The device parameters for CZTS TFSCs as a function of different CdS buffer thicknesses will be discussed in next section.

Relationship between Device Performances and Parameters as a Function of CdS Buffer Thickness. The aforementioned experimental results yielded information about the strong dependence of device performances of CZTS TFSCs on CdS buffer thickness. The observed tendency may be caused by the following:<sup>49,51</sup> (i) recombination rate at the CdS/CZTS interface, (ii) decreased  $R_s$ , and (iii) change in the values of the CBO or valence band offset (VBO) at the CdS/CZTS interface.

For change in the values of the CBO at the CdS/CZTS interface as a function of CdS thickness, we calculated the CBO and VBO at the CdS buffer/CZTS interface as a function of CdS thickness through the measured band gap energies of CdS buffers, literature surveys on the band alignment of CdS buffer/ CIGS with different CdS thicknesses, and the band structure of CZTS. Figure S1 shows (a) the band gap energies of CdS and (b) the calculated CBO and VBO between the CdS/CZTS interfaces as a function of different CdS thicknesses. Table S1 summarizes the detailed values of band gap energies,  $E_{CBM}$  –  $E_{\rm F'}$  CBO,  $E_{\rm F} - E_{\rm VBM}$ , and VBO at CdS/CZTS interfaces as a function of CdS thickness. The band gap energies of CdS prepared on glass substrates decreased from 3.3 to 2.3 eV with increasing CdS thickness. The slightly wide band gap energies of CdS below 25 nm were related to the quantum size effect from nanosized grains of the CdS thin film. At the initial growth stage of CdS by chemical bath deposition at relatively low temperature, the nucleation process is more dominant than the growth process, indicating that the size of grains is below 5 nm.<sup>52,53</sup> On the basis of this reason, the band gap energies showed the values more than 3.0 eV at a film thickness below 25 nm. Figure S1b shows the calculated VBO values, which are not significantly changed because the VBM positions are not changed regardless of CdS thickness. However, the calculated CBO values decreased from +0.6 to -0.40 eV with increasing CdS thickness. On the basis of the above discussion, the values

of CBO may be adjusted by controlling the CdS thickness. The detailed calculation process can be found in the Supporting Information.

The recombination rate at the CdS/CZTS interface and  $R_s$  can be demonstrated by calculating device parameters using single-diode equations (eqs 1 and 2). To clearly demonstrate the relationships between device performances, parameters, and interface conditions in the CdS buffer/CZTS heterojunction, we calculated the device parameters obtained from the best performance cell among each solar cell under different thicknesses of the CdS buffer. Figure 7 shows the device



**Figure 7.** Device parameters obtained from the light J-V curve and device performances of CZTS TFSCs with different thicknesses of CdS buffer: (a)  $J_{0'}$ , A, FF, and  $E_g/q - V_{oc}$  and (b)  $R_{s'}$ ,  $G_{sh'}$ ,  $\eta$ , and  $J_{sc'}$ . All of the data were collected in the best efficiencies of solar cells as a function of CdS thickness.

Table 2. Device Characteristics of CZTS and CZTSSe TFSCs and Their Comparison with the Best Reported CZTSSe TFSCs Using the Hydrazine-Based Process

samples	$J_{\rm sc}$ (mA/cm <sup>2</sup> )	$V_{ m oc}$ (mV)	FF (%)	η (%)	$(eV)^a$	$E_{\rm g}~({\rm eV})/q - V_{\rm oc}~({\rm mV})$	$G_{\rm sh}^{\ \ b}$ (mS/cm <sup>2</sup> )	$\binom{R_s^b}{(\Omega \text{ cm}^2)}$	$A^{b}$	$\int_{o} (mA/cm^2)^b$
48 nm CdS/CZTS	7.46	485	48	1.74	1.49	1005	6.68	5.78	1.98	$8.12 \times 10^{-5}$
62 nm CdS/CZTS	9.14	537	59	2.89	1.51	973	3.47	4.31	1.78	$9.24 \times 10^{-6}$
70 nm CdS/CZTS	15.23	623	61	5.77	1.53	907	2.28	2.14	1.71	$7.81 \times 10^{-6}$
92 nm CdS/CZTS	13.53	624	52	4.22	1.53	906	4.48	2.98	1.89	$2.24 \times 10^{-5}$
123 nm CdS/CZTS	12.76	561	54	3.89	1.52	959	4.71	3.47	1.81	$2.13 \times 10^{-5}$
70 nm CdS/CZTSSe <sup>c</sup>	34.54	494	51	8.77	1.16	666	2.14	2.12	1.52	$4.73 \times 10^{-6}$
solution (hydrazine, Se	35.2	513.4	69.8	12.6	1.13	617	1.61	0.72	1.45	$7.0 \times 10^{-8}$

<sup>*a*</sup>Band gap energies were obtained from the plot of  $(\ln(1 - EQE))^2$  vs energy in the Supporting Information (Figure S4). <sup>*b*</sup>Light shunt conductance  $(G_{sh})$ , series resistance  $(R_s)$ , ideal factor (A), and reverse saturation current density  $(J_0)$  were calculated from the J-V curve under light conditions. <sup>*c*</sup>All of the performance and parameters are taken from the CZTSSe TFSC with a 70 nm thick CdS buffer. <sup>*d*</sup>All of the performance and parameters are taken from the hydrazine-based CZTSSe TFSC reported by IBM researchers. <sup>10</sup>

parameters from the light J-V curve and device performance of CZTS TFSCs as a function of CdS thickness: (a)  $J_{0}$ , A, FF, and  $E_g/q - V_{oc}$  and (b)  $R_{s}$ ,  $G_{sh}$ ,  $J_{sc}$ , and  $\eta$ . Additionally, the values of  $E_{\sigma}^{\circ}$  in the CZTS absorber layers were obtained from the plots of  $(ln(1 - EQE))^2$  versus energy shown in Figure S4. Device performance and parameters of the CZTS solar cells with different CdS buffer thicknesses are summarized in Table 2. All of the solar cell devices show  $V_{oc}$ -deficit characteristics, which are closely related to the recombination rate at the CdS buffer/ kesterite interface.<sup>14,15</sup> Interestingly, we observe a similar relationship between the device performance and parameters. The device parameters including  $J_{0}$ , A,  $R_{s}$ , and  $G_{sh}$  (and notably not including  $E_g/q - V_{oc}$ ) are improved up to a CdS buffer thickness of 70 nm, whereas they deteriorate at larger CdS thickness. The  $V_{0c}$ -deficit in the solar cells is improved up to a CdS buffer thickness of 92 nm and then deteriorated at a thicker CdS buffer layer. The tendencies of FF,  $J_{\rm sc}$  and  $\eta$  are opposite to those of  $J_0$ , A,  $R_s$ ,  $E_g/q - V_{oc}$ , and  $G_{sh}$ . The values of  $E_{\rm g}/q - V_{\rm oc}$  and device parameters such as  $J_0$  and A with a CdS buffer thickness are reduced up to 70 nm.

Another possible reason for the enhanced performance and parameters is the reduced value of both CBO and VBO at the CdS/CZTS interface with increasing thickness of the CdS layer. The previous literature surveys for band alignment at buffer compounds such as CdS, Zn(O,S), ZnO, (Zn,Sn)O, and  $In_2S_3$ buffer-/thin-film-based absorber materials such as kesterite, CdTe, and CIGS heterojunction interfaces suggested that the CBO and VBO values for the buffer/absorber interface can be controlled by adjusting the thickness owing to the quantum size effect and the band gap engineering in the buffer.<sup>48</sup> The values of CBO and VBO decreased with increasing thickness of buffer and the device performances were dramatically worse at negative or highly positive values of CBO conditions.<sup>48</sup> On the basis of the above discussion point, we assume that a causal relationship between the conditions at the CdS/CZTS interface (values of CBO and VBO) can be adjusted by controlling the thickness of the CdS buffer. In the case of a relative thin buffer layer, the values of the CBO and VBO at the CdS/CZTS interface are highly positive (spike type), indicating that the interface acts as a barrier to the generated charge carrier flow, leading to the poor performance.<sup>33</sup> With increasing thickness of the CdS buffer, the values of the CBO and VBO decrease, leading to the enhanced performance. The deteriorated performance of the devices with the CdS buffer thickness greater than 92 nm is attributed to the higher Rs and the negative values of CBO and VBO. The resistivity of the

chemically deposited CdS buffer is more than  $10^4 \Omega$  cm because it consists of nanoscale grains and contains many O and OH species. This higher resistivity of the CdS buffer leads to the higher  $R_{\rm s}$  and lower  $J_{\rm sc}$  and  $\eta$ . The increased  $G_{\rm sh}$  in the thicker CdS buffer is attributed to the nonuniform microstructure consisting of a few nanoscale grains and large grains more than 200 nm in size, which is formed by the mixed mechanism over long reaction times. Previous papers on the growth of chemically deposited metal-sulfides-based buffer on the absorber layers report the nonuniform microstructure consisting of different sized grains for long reaction times and high reaction temperatures.<sup>48,55,56,63,64</sup> Additionally, the negative values of CBO and VBO at thicker CdS buffer produce a cliff-type band alignment between CdS and CZTS, which leads to the loss of  $V_{\rm oct}^{-48}$ 

Performance through Applying 70 nm Thick CdS to the CZTSSe Absorber. To improve the efficiency of kesteritebased TFSCs, we further apply the compositional ratio of (S/(S+ Se)) in the kesterite layer because the band gap energy near 1.1-1.2 eV shows the best performance, even though the best theoretical performance is expected at a band gap energy of 1.5 eV.<sup>14,15</sup> The compositional ratios of the CZTSSe absorber layer are Cu/(Zn + Sn) = 0.57, Zn/Sn = 1.6, and Se/(S + Se) = 0.89, as measured by XRF. The Se-rich CZTSSe absorber thin film shows a dense microstructure consisting of submicron grains and many voids located near the Mo back contact. No secondary phases were observed in the XRD pattern or Raman spectrum, and the cross-sectional FE-SEM images are shown in Figure S5. Figure 8 shows the (a) J-V curve, (b) EQE spectrum and integrated current from the EQE graph, and a (c) plot of  $(\ln(1 - EQE))^2$  versus energy of the most efficient CZTSSe TFSC. The solar cell has a PCE of 8.77% with an active area of 0.30 cm<sup>2</sup> under an AM 1.5G illumination. The performance parameters of the CZTSSe TFSC with the best efficiency are as follows:  $V_{\rm oc}$  = 494 mV, FF = 51%, and  $J_{\rm sc}$  = 34.54 mA/cm<sup>2</sup>. The value of the FF in the CZTSSe TFSC is quite low as compared to that of the kesterite-based TFSCs with a PCE greater than 10%. The EQE spectrum of the CZTSSe solar cell shows an EQE more than 75% in the visible region and decreased EQE in the high wavelength region. The estimated band gap energy from the EQE spectrum in the CZTSSe solar cell is approximately 1.06 eV. Although the CZTSSe TFSC with a 70 nm CdS buffer layer showed an efficiency more than 8%, the tendency of performance was quite different from those of CZTS TFSCs.



**Figure 8.** (a) J-V curve, (b) EQE spectrum and integrated current from the EQE graph, and (c) plot of  $(\ln(1 - EQE))^2$  vs energy of the best efficient CZTSSe TFSCs after process optimization. The compositional ratios of the CZTSSe thin film are Cu/(Zn + Sn) = 0.57, Zn/Sn = 1.6, and Se/(S + Se) = 0.89 under annealing condition at 520 °C for 10 min.

The performance of CZTSSe TFSCs was improved from 8.8 to 10% with decreasing thickness of CdS from 70 to 25 nm because of the enhanced amount of light to the absorber layers. (Data are not shown here.) They were saturated over a 70 nm thick CdS buffer layer. The difference behavior about device performances as a function of different thicknesses for the CdS buffer layer between CZTS and CZTSSe may be attributed to the difference in their roughness, band alignment between CdS and the absorber, and thickness of the absorber. The performance and parameters of the most efficient CZTSSe solar cell and the previously reported CZTSSe solar cell using a hydrazine-based process are summarized in Table 2 to clearly illustrate the poor performance. The difference in FF and  $V_{\rm oc}$ deficit is clearly observed between the present results (51% and 666 mV) and the previously reported CZTSSe solar cell (69.8% and 617 mV). Furthermore, the device parameters such as  $G_{\rm sh}$  $R_{\rm s}$ , A, and  $J_0$  for the present results ( $G_{\rm sh}$ : 2.14 mS/cm<sup>2</sup>,  $R_{\rm s}$ : 2.12  $\Omega$  cm<sup>2</sup>, A: 1.52, and  $J_0$ : 4.73 × 10<sup>-6</sup> mA/cm<sup>2</sup>) are higher than those of the previously reported CZTSSe solar cell ( $G_{\rm sh}$ : 1.61 mS/cm<sup>2</sup>,  $R_s$ : 0.72  $\Omega$  cm<sup>2</sup>,  $\bar{A}$ : 1.45, and  $J_0$ : 7.0 × 10<sup>-8</sup> mA/cm<sup>2</sup>). Particularly, the values of  $R_s$  and  $G_{sh}$  in the present results are 3 and 1.5 times higher, respectively, than those of the previously

reported CZTSSe solar cell. Our previous paper on CZTSSe solar cells showed the presence of secondary phases and voids at the interface between the CZTSSe absorber layer and the Mo back contact, which led to the lower values of the device parameters. The  $V_{\alpha}$ -deficit characteristic of the present solar cell is higher than that of the previously reported CZTSSe solar cell in spite of having similar  $J_{sc}$  values and optical band gap energies. This  $V_{\rm oc}$ -deficit characteristic, caused by the higher recombination rate at the buffer/absorber interface and the low minority charge lifetime, is evidence of higher defect densities on the CZTSSe surface in the present cell than in the previously reported CZTSSe TFSC. On the basis of these comparisons, the poor performance in the present case compared to that previously reported is attributed to the presence of unexpected secondary phases, voids, and higher defect densities on the CZTSSe surface. This implies that the performance of our CZTSSe TFSC can be improved by controlling the defect densities on the kesterite surface through surface modification using alkali elements and by removing the secondary phases and voids near the Mo back contact using optimized annealing parameters.

#### CONCLUSIONS

CdS buffer/CZTS heterojunction solar cells have been successfully fabricated by systematically studying the relationship between the device performance and device parameters as a function of different CdS buffer thicknesses. An 8.8% efficiency is achieved by applying 70 nm thick CdS buffer to the CZTSSe absorber layer. All aspects of device performance except for that related to  $V_{oc}$  are enhanced with increased CdS buffer thickness up to 70 nm and are diminished with thicker CdS buffer thickness. The V<sub>oc</sub>-deficit improves with increased CdS buffer thickness up to 92 nm and then deteriorates with greater CdS buffer thickness. The tendencies of FF,  $J_{\rm sc\prime}$  and  $\eta$ are opposite to those of  $J_{0}$ , A,  $R_{s}$ ,  $E_{g}/q - V_{oc}$ , and  $G_{sh}$ . These tendencies synergistically affect the recombination rate at the CdS/CZTS interface and the microstructure of the CdS to a degree dependent on the CdS buffer thickness. We believe that this detailed systematic study is useful for deeper insight into the relationship between the device performance and device parameters as a function of CdS buffer thickness.

#### ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b09266.

Band gap energies of CdS with different thicknesses, the CBO and VBO values at CdS buffer/CZTS interfaces as a function of CdS thickness through literature surveys, images of a reaction solution during the CdS deposition, images of CdS thin films on the CZTS and SLG substrates, Raman spectra of CZTS thin films using different wavelengths such as 325 and 623 nm, FE-SEM images of full-structured CZTS TFSCs devices, band gap energy plots of CdS/CZTS heterojunction solar cells as a function of CdS thickness, XRD, Raman spectrum of the CZTSSe thin film, and FE-SEM images of CZTSSe devices (PDF)

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#### Notes

The authors declare no competing financial interest.

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