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Improving the Back Electrode Interface Quality of Cu₂ZnSn(S,Se)₄ Thin-Film Solar Cells Using a Novel CuAlO₂ Buffer Layer

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Supporting Information



ABSTRACT: A novel buffer layer CuAlO₂ (CAO) with smooth and compact surface was applied in $Cu_2ZnSn(S,Se)_4$ -based (CZTSSe) solar cells to optimize back electrode interface (BEI). It is found that introduction of CAO exerts a remarkable effect on the crystalline quality of absorber and the thickness of interfacial layer $Mo(S,Se)_2$ (MSSe) at BEI. When the thickness of CAO buffer layer was optimized to 10.6 nm, CZTSSe film exhibits preferable crystallinity with larger grains without pin holes. Also, MSSe decreases significantly to \sim 244 nm, and it is smaller than that (\sim 463 nm) of the sample without CAO. With this interface optimization, the solar cell with 10.6 nm thick CAO shows the higher shunt resistance, lower reversion saturation current density and smaller series resistance, leading to an increase in short-circuit current density (from 26.91 to 30.66 mA cm^{-2}) as well as fill factor (from 46.60% to 49.93%) compared to that of the sample without CAO. As a consequence, power conversion efficiency of the corresponding devices increases from 4.12% to 5.10%. The influence mechanism of CAO buffer layer on the photovoltaic properties of CZTSSe solar cell is discussed in detail, and this approach presents a wide range of possibilities for the further development of interface optimization in solar cells.

KEYWORDS: $Cu_2ZnSn(S,Se)_4$ solar cell, CuAlO₂ buffer layer, smooth and compact surface, back electrode interface, crystalline quality, interface optimization, power conversion efficiency

1. INTRODUCTION

Research in the energy field is a hit in recent years, among which one of the most promising orientations is solar cells due to its eco-friendly and abundant feature. $Cu_2ZnSn(S,Se)_4$ (CZTSSe) compound with a kesterite structure possesses an adjustable band gap (E_g) of 1.0–1.5 eV and a large absorption coefficient (α) of over 10⁴ cm⁻¹, showing great advantages in fabricating high-performance solar cells.¹⁻³ Therefore, it has been attracting a lot of interest. In addition, CZTSSe is nontoxic, inorganic and comprised of inexpensive constituent element, facilitating its large-scale production in regard to industrial prospect. Up to now, the world-record power

conversion efficiency (PCE) of CZTSSe devices fabricated by IBM group is 12.6%;⁴ however, it is still rather far from the requirement for commercialization and much lower than that of the counterpart Cu(In,Ga)Se₂ (CIGS) solar cell.⁵

It is commonly known that one of the major barriers to impede CZTSSe solar cell is the imperfect back electrode interface (BEI).⁶ According to thermodynamic calculations,⁶ both absorber and Se vapor may react with Mo electrode

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Figure 1. Schematic diagram of the device structure and the energy band alignment of p-CAO/p-CZTSSe heterojunction.

during selenization process (SEP), and as a result some undesirable phases (see reaction 1) are generated at the Mo/ CZTSSe interface.

$$2Cu_2ZnSnS_4 + Mo \xrightarrow{SLP} 2Cu_2(S, Se) + 2Zn(S, Se) + 2Sn(S, Se) + Mo(S, Se)_2$$
(1)

These secondary phases cut down the absorber crystalline quality and aggravate the recombination at Mo/CZTSSe interface. In SEP, Sn(S,Se) is liable to get away because of its high volatility,⁷ leaving voids at Mo/CZTSSe interface. Diffusion of Cu into the absorber bottom and $Mo(S,Se)_2$ (MSSe) causes the same problem, too.^{4,8,9} As a result, due to the shunt paths (voids, pin holes, and so forth.) produced during the formation of secondary phases, the carrier transportation might be blocked.⁹ Notably, the role of MSSe is bidirectional. On the one hand, it facilitates an electrical quasi-ohmic contact and strengthens the adhesion of CZTSSe to Mo electrode due to its high work function; on the other hand, it is adverse in terms of the high series resistance (R_s) caused by thick MSSe. To minimize the issues above, considerable efforts have been devoted. For example, Liu et al.¹⁰ employed TiB₂ interlayer layer at BEI and found that it reduced R_s from 22.0 to 10.3 $\Omega \cdot cm^2$, but led to the deterioration on device performance. Scragg et al.¹¹ applied a TiN layer to impede the decomposition of CZTS and indicated that it can passive Mo/CZTS interface indeed, unfortunately, also caused a higher R_s. Additionally, ZnO,^{12,13} $Na_2S_1^{14} Al_2O_3^{15,16} C_2^{17}$ and Ti^{18} materials were utilized at BEI, too.

 $CuAlO_2$ (CAO) is a p-type transparent conducting oxide (TCO) with good chemical and thermal stability, and its crystal is generated under the temperature exceeding 900 °C.¹⁹ Then, the probable reaction between CZTSSe, Mo, and CAO layer can be prevented. Generally, CAO grown at room temperature is amorphous with smooth and compact surface,^{19,20} which provides less nucleation center of overlying absorber (see Figure 1), then facilitates the formation of CZTSSe film with larger grains and fewer defects. However, the as-grown amorphous CAO exhibits a poor conductivity (almost insulating), being beneficial for interfacial defects passivation via optimizing its thickness. Besides, Fleischer et al.²¹ reported that p-type TCOs can act as electron blocking or hole transport layers in thin-film solar cells. The valence-bands of CAO and CZTSe lie at 5.20 and 5.70 eV below the vacuum level, respectively.²²⁻²⁶ Electron affinity and work function of CAO are 1.70 and 4.74 eV, and the corresponding values were taken to be 4.70 and 5.34 eV for CZTSe, respectively.²²⁻²⁶ Consider that the E_g difference between CZTSe and high-

selenized CZTSSe (1.063 eV for CAO#0 and 1.053 eV for CAO#2 in this work) is approximate. Thus, the corresponding parameter of CZTSe was adopted to display the band alignment of CAO/CZTSSe interface. As shown in Figure 1, a hole barrier (0.5 eV) formed at CAO/CZTSSe interface, which is not good to the carrier collection of Mo electrode. However, the photoinduced hole could tunnel this barrier, when CAO buffer layer is deposited to be thin enough (smaller than 20 nm). In addition, it should be noted that an electron barrier (3.0 eV) is also observed.^{22–26} Consequently, recombination of BEI can be minimized via preventing electron transport from absorber to Mo electrode, being favorable to the J_{SC} improvement. To date, there are no studies devoted to the application of CAO as a buffer layer in CZTSSe-based solar cells. In this study, an ultrathin CAO layer was introduced into BEI, and its influence mechanism on the photovoltaic performance of CZTSSe solar cell was discussed in detail.

2. EXPERIMENTAL SECTION

2.1. Preparation of CAO Layer on Mo-Coated Soda Lime Glass (SLG/Mo). CAO thin films were deposited on SLG/Mo substrates using radio frequency (RF) magnetron sputtering with argon as the work gas at a power of 40 W and pressure of 1.0 Pa. The growth rate of CAO film is estimated to be 7.98 nm·min⁻¹ observed in Figures S1 and S2. By controlling deposition time, a series of CAO thin films with the thickness of 0, 7.9, 10.6, 13.3, 15.9, and 18.6 nm were deposited on SLG/Mo substrates.

2.2. Absorber Preparation. CZTSSe films were prepared by a two-step procedure. First, CZTS precursor solution was obtained by dissolving Cu(CH₃COO)₂·H₂O (1.1979 g), SnCl₂·2H₂O (0.8462 g), ZnCl₂ (0.5993 g), and (NH₂)₂S (2.2836 g) into 10 mL of dimethyl sulfoxide (DMSO), and then magnetically stirring for 2 h at 55 °C. Subsequently, spin-coating the precursor solution on the SLG/Mo/ CAO substrate to prepared CZTS precursor films. The rotating rate is 800 rpm for 5 s and then 3000 rpm for 30 s, followed by roasting at 300 °C for 3 min in N2 atmosphere, then it is dried to room temperature. The coating and drying steps were repeated 10 times to prepare CZTS precursor films with desired thickness. Second, the asprepared CZTS films and 100 mg of selenium granule were sealed in graphite box (diameter, 55 mm; volume, 40 mL), followed by a selenization process with annealing conditions of 550 °C for 15 min. The 70 mL/min nitrogen flow was applied during selenization process.

2.3. Devices Fabrication. CZTSSe solar cells were prepared with a structure of SLG/Mo/CAO/CZTSSe/CdS/i-ZnO/indium tin oxide (ITO)/Al grid, as shown in Figure 1. Buffer layer CdS (~50 nm) was prepared by chemical bath deposition (CBD) method. CdSO₄ and $(NH_2)_2S$ were used as Cd and S sources, respectively. By controlling deposition time, the CdS film with desired thickness was prepared on the surface of CZTSSe at alkaline solution realized via adding



Figure 2. (a) XRD patterns of CZTSSe films grown on the SLG/Mo/CAO substrates with different T_{CAO} . (b) High-magnification view of the (112) peak corresponding to CZTSSe, and its fwhm variation against T_{CAO} is also depicted in the inset. (c) Raman spectra from 532 nm excitation of CZTSSe films with different T_{CAO} . (d) Raman spectra comparison between CAO#2 (red) and CAO#0 (blue).

appropriate NH₃·H₂O. Notably, NH₄Cl was utilized as complexing agent. Sequentially, i-ZnO (~50 nm) and ITO (~260 nm) window layers were deposited on the surface of CdS by RF magnetron sputtering. Finally, Al grids were used as the top contact by thermal evaporation, and the whole device was scribed mechanically into 9 small cells with an active area of 0.19 cm². The thickness of CAO buffer layer (T_{CAO}) in these devices is 0, 7.9, 10.6, 13.3, 15.9, and 18.6 nm and the corresponding solar cells are denoted as CAO#0, CAO#1, CAO#2, CAO#3, CAO#4, and CAO#5, respectively. For convenience, the SLG/Mo/CAO/CZTSSe films of these cells are also marked as the same symbols above.

2.4. Films and Devices Characterizations. The crystal structures were characterized by X-ray diffraction (XRD) using a DX-2700 X-ray diffractometer equipped with Cu K α radiation (λ = 1.5406 Å). The Raman spectra were carried out by HoribaJobin Yvon HR800 confocal Raman system (532 nm and 50× objective lens). The focused spot size was selected to be the order of 1 μ m with an excitation power of 0.5 mW. At these experimental conditions, laserinduced heating²⁷ can be excluded. Morphology of surface and crosssection were characterized by HITACHI S-4800 field-emission scanning electron microscopy (FE-SEM) equipped with an energydispersive X-ray spectroscopy (EDS) system (EDAX Genesis 2000). Current density-voltage curves were measured with a Keithley 2400 source meter under simulated AM 1.5G solar illumination, as calibrated with an official certified crystalline Si reference cell. External quantum efficiency curves were measured using a Zolix SCS100 QE system equipped with a 150 W xenon light source, a lockin amplifier, and an integrating sphere. Capacitance-voltage characteristics were recorded using a KEITHLEY 4200-SCS in the -1.0 to +1.0 V dc voltage region with 20 mV rms as the test acvoltage (frequency = 100 kHz).

3. RESULTS AND DISCUSSION

In order to characterize the effect of CAO buffer layer on the crystallinity, phase constitution and morphology of CZTSSe films, measurements including XRD, Raman, and SEM were carried out. Figure 2a depicts XRD patterns of CZTSSe films grown on the SLG/Mo/CAO substrates with different T_{CAO} .

All XRD peaks can be indexed to kesterite CZTSSe except for the (110) and (211) peaks of Mo,^{28,29} no XRD peaks assigned to unfavorable secondary phases of Cu_xSe , ZnSe, and Cu_2SnSe_3 were observed. To better evaluate the CAO influence on the absorber crystallinity, full-width at halfmaximum (fwhm) of (112) peak against T_{CAO} were plotted in Figure 2b. Evidently, fwhm decreases first when T_{CAO} increases from 0 to 10.6 nm and reaches a minimum value under the $T_{\rm CAO}$ of 10.6 nm, however, increases gradually as $T_{\rm CAO}$ sequentially increases up to 18.6 nm. The variation indicates that the crystal quality of absorber increases with T_{CAO} of 0-10.6 nm due to the smooth and compact surface of CAO, 19,20 while decreases with T_{CAO} of 10.6–18.6 nm, which is possibly attributed to the stronger blocking effect for Na diffusion by relatively thick CAO. In conclusion, CAO#2 is of superior crystal quality, and it is crucial to optimize T_{CAO} to maintain its positive effects.

It is well-known that the presence of ZnSe, ZnS, and Cu₂SnSe₃ impurities cannot be distinguished by XRD measurement since their major diffraction peaks overlap with those of kesterite CZTSSe.^{30,31} Therefore, to further confirm the phase constitution of CZTSSe films, Raman spectra were conducted with a 532 nm laser excitation line, as shown in Figure 2c. Five peaks are observed at 174, 196, 231, 250, and 329 cm^{-1} . The peaks located at 174, 196, and 231 cm⁻¹ are in agreement with well-known vibrational characteristics of kesterite CZTSSe.^{32,33} Note that the intensity of 196 cm⁻¹ peak (vibration peak of Se ion) is much higher than that of 329 cm⁻¹ peak (vibration peak of S ion), indicative of a small amount of S involved in absorber.³⁴ Remarkably, a weak peak situated at \sim 250 cm⁻¹ corresponding to binary ZnSe is found in the spectra.^{35,36} To further investigate the impact of CAO buffer layer on the ZnSe phase quantity in absorber, spectra of CAO#0 and CAO#2 were selected for comparison. As observed from Figure 2d, the intensity of the 250 cm⁻¹



Figure 3. Surface morphology of CZTSSe films grown on SLG/Mo/CAO substrates with T_{CAO} of (a) 0, (b) 7.9, (c) 10.6, (d) 13.3, (e) 15.9, and (f) 18.6 nm, respectively.



Figure 4. Cross-sectional SEM images of (a) CAO#0, (b) CAO#2, and (c) CAO#5.

mode of CAO#2 is weaker compared to CAO#0, implying that the existence of CAO buffer layer has suppressed the formation ZnSe phase. As we all know, atomic ratio of CZTS film is inclined to be out of equalized through SEP, which is attributed to the escape of SnSe due to its high volatility and the migration of Cu into BEI owing to its high diffusivity.^{4,7-9} Thus, the related phases (Cu_xSe, ZnSe, and so forth) are likely to be formed in absorber and Mo/CZTSSe interface under the Se-rich vapor of SEP. The decreased ZnSe in CAO#2 might be due to the superior atomic ratio of absorber, which is induced by the application of CAO buffer layer with smooth and compact surface, because the Se vapor penetration, reaction between Mo, and absorber can be partially blocked. Also, the 250 cm⁻¹ vibration peak may be assigned to amorphous selenium (a-Se)^{27,37} because of the possible floating Se powder on the absorber surface. The decreased ZnSe phase in absorber is conducive to increase the shunt resistance $(R_{\rm Sh})$ of device (discussed later). Besides, it is observed that the 196 cm^{-1} peak of CAO#2 exhibits smaller fwhm (~5235 cm⁻¹) in comparison with that (~6185 cm^{-1}) of CAO#0, suggesting a better crystalline quality. This result is consistent with XRD findings.

Figure 3a-f displays the surface morphologies of three typical CZTSSe films grown on SLG/Mo/CAO substrate with T_{CAO} of 0, 7.9, 10.6, 13.3, 15.9, and 18.6 nm, respectively. The CZTSSe films with T_{CAO} of 10.6, 13.3, and 15.9 nm (CAO#2-4) show more compact morphology without pin holes and

larger grains than that of CAO#0, which is possibly attributed to the smooth and compact surface of CAO (see Figure 1).^{19,20} However, the grains become smaller as T_{CAO} exceeded 15.9 nm, as shown in Figure 3f. This phenomenon is also observed from the work of Liu et al.,¹⁰ where the crystallinity of absorber became worse when the TiB₂ intermediate layer increased from 10 to 70 nm. They attributed this phenomenon to the lack of Na in absorber caused by the inhibition of the relatively thick and continuous TiB₂ layer for Na diffusion from SLG.^{38,39} Therefore, the crystalline quality deterioration in CAO#4 and CAO#5 was probably due to the same reason. In addition, it should be noted that the larger grains and less grain boundaries can reduce the chance of photoinduced carriers being trapped, which is favorable for device performance (discussed later). Figure 4a-c shows the cross-sectional SEM images of CAO#0, CAO#2, and CAO#5, respectively. MSSe (~463 nm) layer of CAO#0 is observed at BEI. Interestingly, it decreases significantly to ~244 nm for CAO#2 and ~61 nm for CAO#5, respectively. This result implies that the interfacial layer MSSe growth has been suppressed by employing CAO buffer layer into BEI, moreover, thicker CAO leads to stronger suppression. The thinner MSSe lowers down the R_{s} , which is helpful to obtain higher PCE. Additionally, it is also revealed from Figure 4 that CAO#2 has the largest grain size, hinting that ultrathin CAO layer (10.6 nm) blocked Na diffusion slightly from SLG into the absorber. Nevertheless, the blocking



Figure 5. (a) J-V curves of CAO#0 and CAO#2 under AM 1.5G illumination. (b) EQE curves and the integrated J_{SC} (inset) of CAO#0 and CAO#2. (c) Plots of J_{SC} , FF, J_0 , R_S/R_{Sh} and R_S/A as a function of $T_{CAO.}$ (d) E_g of CAO#0 and CAO#2 calculated from EQE data.

effect of CAO layer gets severe when T_{CAO} reaches 18.6 nm, leading to the fine grains, as shown in Figure 4c. This result is in accordance with the corresponding surface morphologies.

Figure 5a illustrates the photocurrent density–voltage (J-V) curves of CZTSSe solar cells with and without 10.6 nm thick CAO buffer layer under AM 1.5G illumination. As indicated, the PCE increased from 4.12% (CAO#0) to 5.10% (CAO#2), which mainly results from an improvement in J_{SC} (from 26.91 to 30.66 mA·cm⁻²) and FF (from 46.60% to 49.93%). The gain in J_{SC} and FF can be ascribed to the decrease in J_0 and R_s , and increase in $R_{\rm Sh}$ on account of the thinner MSSe and better absorber quality. Furthermore, it is reported that the crossover point between the light and dark J-V curves means the presence of a back contact barrier.⁴⁰ In our cases, the crossover point of CAO#2 corresponds to a higher current density, suggesting a lower back barrier height and a smaller R_s accordingly compared to that of CAO#0.

Table 1 summarizes the photovoltaic parameters of CZTSSe solar cells with different T_{CAO} , which is determined by fitting the J-V data with one-diode model.⁴¹ It is found that the PCE first increased with increasing T_{CAO} and then decreased. The maximum PCE (CAO#2) was obtained when applied a 10.6 nm thick CAO layer into Mo/CZTSSe interface. Also, CAO#2 undergoes a considerable enhancement in nearly all the

Table 1. Photovoltaic Parameters of CZTSSe-Based Solar Cells with Different Thickness of CAO Buffer Layer

cell	$T_{\rm CAO}~({\rm nm})$	$V_{\rm OC}$ (V)	$J_{\rm SC}~({\rm mA}{\cdot}{\rm cm}^{-2})$	FF (%)	PCE (%)
CAO#0	0	0.328	26.91	46.60	4.12
CAO#1	7.9	0.325	26.63	46.37	4.01
CAO#2	10.6	0.333	30.66	49.93	5.10
CAO#3	13.3	0.339	28.60	50.05	4.85
CAO#4	15.9	0.336	27.38	49.94	4.60
CAO#5	18.6	0.296	27.69	43.77	3.58

photovoltaic parameters. In particular, CAO#2 has the lowest $R_{\rm S}$ and reversion saturation current density (J_0) and the highest $R_{\rm Sh}$ due to the thinner MSSe and superior absorber quality, as a consequence, inducing the optimal $J_{\rm SC}$ and higher FF, which gives rise to an overall increase in PCE by ~24% compared to that of the solar cell without CAO layer. Table 2 displays the electrical parameters including $R_{\rm S}$, $R_{\rm Sh}$, diode quality factor (n), J_0 , $R_{\rm S}/R_{\rm Sh}$ and $R_{\rm S}/n$. The changes of $R_{\rm S}/R_{\rm Sh}$, $R_{\rm S}/n$, J_0 as well as $J_{\rm SC}$ and FF with $T_{\rm CAO}$ are illustrated in Figure 5c. It is known that FF is mainly associated with $R_{\rm S}$ and $R_{\rm Sh}$. Higher FF can be obtained by the smaller $R_{\rm S}$ and larger $R_{\rm Sh}$, namely, the lower $R_{\rm S}/R_{\rm Sh}$ leads to an increase in FF. As plotted in Figure 5c, three samples with 10.6, 13.3, and 15.9 nm thick CAO have the relatively lower $R_{\rm S}/R_{\rm Sh}$ and apparently higher FF. Moreover, $J_{\rm SC}$ can be denoted as the following equation^{42,43}

$$\left(1 + \frac{R_{\rm S}}{R_{\rm Sh}}\right) J_{\rm SC} = J_{\rm ph} - J_0 (e^{qR_{\rm S}J_{\rm SC}/nKT} - 1)$$
(2)

where $J_{\rm ph}$ is photogenerated current density, q (1.6 × 10⁻¹⁹), K, and T represent electron charge, Boltzmann constant, and temperature, respectively. Clearly, the lower the $R_{\rm S}/R_{\rm Sh}$ and J_0 are, the higher the $J_{\rm SC}$ is. As shown in Figure 5c, the $R_{\rm S}/R_{\rm Sh}$ value changes slightly (from 0.0031 to 0.0085) and is much smaller than 1. Consequently, based on the eq 2, we consider that the increase or decrease in $J_{\rm SC}$ results from decreased or increased J_0 and $R_{\rm S}/n$. In addition, $R_{\rm S}/n$ mainly depends on $R_{\rm S}$ since the *n* varies subtly in our case, too. Thus, for CAO#2, we conclude that the lowest $R_{\rm S}$ and J_0 give rise to the highest $J_{\rm SC}$, which is mainly responsible for its higher PCE.

However, the PCE begins to decrease with increasing T_{CAO} from 10.6 (CAO#2) to 18.6 nm (CAO#5), which we will discuss below. One reason is that $R_{\rm S}$ of CAO#5 increased due to the relatively thick CAO layer. Moreover, its absorber quality became degraded due to the stronger blocking effect for Na diffusion by thicker CAO, which also results in higher $R_{\rm S}$.

Table 2. Electrical Parameters (R_S , R_{Sh} , n, J_0), R_S/R_{Sh} and R_S/n of CZTSSe-Based Solar Cells with Different Thickness of CAO Buffer Layer

cell	$R_{\rm S} \left(\Omega \cdot {\rm cm}^2 \right)$	$R_{\rm Sh} \left(\Omega \cdot {\rm cm}^2 \right)$	n	$J_0 (\mathrm{mA} \cdot \mathrm{cm}^{-2})$	$R_{\rm S}/R_{\rm Sh}$	$R_{\rm S}/n$
CAO#0	2.47	289.58	2.27	9.86×10^{-2}	8.5×10^{-3}	1.09
CAO#1	2.13	326.80	2.37	1.30×10^{-1}	6.5×10^{-3}	0.90
CAO#2	1.49	469.48	2.21	7.34×10^{-2}	3.1×10^{-3}	0.67
CAO#3	1.56	423.73	2.25	7.9×10^{-2}	3.7×10^{-3}	0.69
CAO#4	1.67	434.78	2.40	1.16×10^{-1}	3.8×10^{-3}	0.70
CAO#5	1.70	202.84	2.57	3.00×10^{-1}	8.3×10^{-3}	0.66



Figure 6. Plots of (a) C^{2-} versus V and (b) carrier density (N_A) versus the distance to the junction for CAO#0 (blue) and CAO#2 (red), respectively.

The other is that smaller grains cause a decrease in $R_{\rm Sh}$ and increase in J_0 . As a consequence, these two factors drag down $J_{\rm SC}$ and FF, thus, the PCE becomes deteriorated (3.58%). To sum up, it is crucial to optimize the $T_{\rm CAO}$ so as to maintain its positive effects on device performance.

To further confirm the J_{SC} improvement after introducing CAO buffer layer, EQE measurement for CAO#0 and CAO#2 were carried out, as illustrated in Figure 5b. As compared with CAO#0, EQE of CAO#2 increases greatly in entire visible and part of infrared regions, demonstrating its better collection efficiency or segregation ability of photogenerated carrier. Note that EQE represents the density ratio between photoinduced carriers to incident photons, then, the J_{SC} can be estimated by integrating EQE data over the entire spectrum combining eq 3 below, as shown in the inset of Figure 5b

$$J_{\rm SC} = q \int_0^\infty F_{\rm 1.5}(\lambda) \cdot E Q E(\lambda) \cdot d\lambda$$
(3)

 $F_{1.5}(\lambda)$ is the incident photons density under AM 1.5G solar illumination, and *q* denotes electronic charge (1.6 × 10⁻¹⁹ C). $J_{\rm SC}$ of CAO#0 and CAO#2 have been calculated to be 26.77 and 29.94 mA·cm⁻², respectively, which is similar to the measured value (see Figure 5a) from the solar simulator.

The E_g of the absorber can be determined from the intercept at the x-axis in the plot of $[hv \cdot \ln(1 - EQE)]^2$ versus hv, where the hv is photoenergy. As displayed in Figure 5d, E_g has been estimated to be 1.063 eV for CAO#0 and 1.053 eV for CAO#2, respectively. Therefore, to some extent, increase in J_{SC} for CAO#2 is supported by its smaller E_g . Indeed, EDX measurement for CZTSSe films corresponded to CAO#0, CAO#2, and CAO#5 was conducted, as displayed in Table S1. It has been found that S/(S + Se) of absorber decreases as CAO thickness increases, which may be attributed to the stronger blocking effect for Se vapor penetration by thicker CAO layer. That is to say, higher selenized CZTSSe films were obtained as inserted thicker CAO buffer layer into BEI. This result also verifies E_g variation.⁴⁴ In addition, it is worthwhile to note that the smaller $E_{\rm g}$ should lead to the lower $V_{\rm OC}$, but actually we have not seen such variations in Table 1. So, there must be the other factors that shift $V_{\rm OC}$ to a higher value. According to the discussion of Figure 2d, for CAO#2, fewer ZnSe secondary phase was formed in absorber compared to CAO#0, then, resulted in bigger $R_{\rm Sh}$, which is partly responsible for the higher $V_{\rm OC}$. Besides, CAO#2 has the weaker bulk recombination due to its increased absorber crystallinity, leading to the increase of $V_{\rm OC}$, too.

Furthermore, in order to compare the segregation ability of photogenerated carrier, capacitance–voltage (C-V) was carried out for CAO#0 and CAO#2 under dark conditions, as shown in Figure 6. The width of the depletion layer (W_d) and the activated carrier density (N_A) of the device were determined combining the equations below^{45,46}

$$\frac{1}{C^2} = \frac{2(V_{\rm bi} - V)}{A_{\rm Cell}^2 \xi_r \xi_o q N_{\rm A}}$$
(4)

$$W_{\rm d} = \sqrt{\frac{2\xi_{\rm r}\xi_{\rm o}V_{\rm bi}}{qN_{\rm A}}} \tag{5}$$

where $V_{\rm bi}$, $A_{\rm Cell}$, and q are the built-in potential, active area of the cell (0.19 cm²) and electronic charge (1.6 × 10⁻¹⁹ C), respectively. $\xi_{\rm o}$ and $\xi_{\rm r}$ are the free space permittivity (generally 8.85 × 10⁻¹² F·m⁻¹) and the relative dielectric constant of CZTSSe, respectively. According to the report of Persson et al.,⁴⁷ $\xi_{\rm r}$ is linearly interpolated from 8.5 to 6.7 with the $E_{\rm g}$ increasing from 1.0 to 1.5 eV; here we took the $\xi_{\rm r}$ value to 8.27 for CAO#0 and 8.31 for CAO#2, respectively (see Figure S3). As shown in Figure 6a, by fitting the plot of $1/C^2$ versus V, $N_{\rm A}$, and $V_{\rm bi}$ are calculated to 7.64 × 10¹⁵ cm⁻³ and 0.95 V for CAO#2, 1.59 × 10¹⁶ cm⁻³ and 0.64 V for CAO#0, respectively. Using eq 5 and the $N_{\rm A}$ and $V_{\rm bi}$ values, the $W_{\rm d}$ of CAO#2 and CAO#0 are calculated to 338 and 191 nm, respectively, as illustrated in Figure 6b. It is well recognized that wider $W_{\rm d}$ enable the segregation of photogenerated carriers and recombination decrease in absorber,^{48,49} then increasing $J_{\rm ph}$ and $J_{\rm SC}$. Therefore, one of the reasons that CAO#2 has bigger EQE or $J_{\rm SC}$ is that it has wider $W_{\rm d}$ than CAO#0, while the other one is that CAO#2 has smaller $R_{\rm S}$ and $J_{\rm 0}$.

4. CONCLUSION

We have employed novel CAO film as a buffer layer between absorber and Mo electrode to improve the back electrode interface quality of Cu₂ZnSn(S,Se)₄ solar cell. The results demonstrate that application of CAO suppresses the reaction between Se vapor, absorber, and Mo electrode, leading to the decreased MSSe interfacial layer and lower R_S accordingly. Also, it is crucial to optimize T_{CAO} to maintain its positive effects. Crystal quality of absorber increases with increasing $T_{\rm CAO}$ from 0 to 10.6 nm due to smooth and compact CAO but decreases as T_{CAO} exceeds 10.6 nm on account of stronger blocking effect for Na diffusion. The optimal PCE was obtained as inserted 10.6 nm thick CAO (CAO#2) into BEI, which is mainly attributed to the increase in J_{SC} and FF. For CAO#2, the increased segregation ability of photogenerated carrier supported by the bigger W_d is partially responsible for its higher J_{SC} . Increase in FF results from the decreased R_S/R_{Sh} that is, smaller R_S due to thinner MSSe layer and preferable absorber crystal quality, and bigger $R_{\rm Sh}$ owing to the improved BEI quality. In summary, the approach that applying smooth and compact buffer layer involved an appropriate energy band alignment for interfacial layers is supposed to be the key role in preparing high performance devices, broadening the possibilities for the further development of interface optimization in CZTSSe-based or other solar cells. Extensions of this interface optimization strategy with CAO are currently underway in our group.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.8b02247.

Cross-section SEM images of CAO films grown on SLG/Mo substrate by controlling depositing time (from 40 to 55 min) and variation in T_{CAO} against sputtering time; plot of ξ_r as a function of E_g and the compositions of the CZTSSe films grown on SLG/Mo/CAO substrates with different T_{CAO} (PDF)

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Notes

The authors declare no competing financial interest.

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