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1 Solution-Processed Pure Sulfide $\text{Cu}_2(\text{Zn}_{0.6}\text{Cd}_{0.4})\text{SnS}_4$ Solar 2 Cells with Efficiency 10.8% Using Ultrathin CuO 3 Intermediate Layer

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7 Herein, it is demonstrated that incorporating an ultrathin p-type cupric oxide
8 (CuO) enhances the performance and stability of solution-processed
9 $\text{Cu}_2(\text{Zn}_{0.6}\text{Cd}_{0.4})\text{SnS}_4$ (CZCTS)/CdS thin film solar cells. In sol-gel CZCTS/CdS
10 thin film solar cells, nanoscale CuO films (4–32 nm) are deposited on top of
11 molybdenum (Mo) by magnetron sputtering and this is used as an intermediate
12 layer (IL). The CuO IL thickness has a significant effect on the short-circuit
13 current density (J_{sc}) in CZCTS/CdS solar cell devices. As a result, a maximum
14 power conversion efficiency (PCE) of 10.77% is measured for the optimized
15 device with 4 nm CuO compared with 10.03% for the reference device without a
16 CuO layer. Furthermore, the stability of the devices is enhanced significantly by
17 incorporating the CuO IL. This work demonstrates that through proper design of
18 the CuO intermediate layer thickness, both the back interface quality and optical
19 property of the CZCTS absorber can be tuned to enhance the device performance.
20

1. Introduction 1

The pure sulfide semiconductor $\text{Cu}_2\text{ZnSnS}_4$ 2
(CZTS) with a kesterite structure is a prom- 3 Q4
ising sustainable light absorber material 4
for next-generation thin film solar cells.^[1–3] 5
Unlike the counterpart chalcopyrite semi- 6
conductors, the CZTS semiconductor is 7
entirely composed of earth-abundant chem- 8
ical elements. Although in principle this 9
opens the possibility of generating electrical 10
power on a grid scale, in practice, the state of 11
development of CZTS photovoltaic devices 12
has been slow. In the past 5 years, there have 13
been no major breakthroughs in certified 14
power conversion efficiency (PCE) of 15
CZTSSe devices.^[4,5] There are two reasons 16
for this. First, the complex CZTS crystalline 17
structure is defect intolerant.^[6] Due to the 18
similarity in ionic radii of the Cu^+ and Zn^{2+} ions, the formation 19
energy of Cu_{Zn} and Zn_{Cu} antisite defects is low and these defects 20

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1 and the associated defect complexes can form readily in large num-
 2 bers in CZTS.^[7] At high concentration, these antisite defects can
 3 cause the symmetry of the CZTS lattice to transform from an
 4 ordered (I-4) to a disordered (I-42m) configuration.^[8] The point
 5 defects resulting from this cationic disorder leads to the formation
 6 of band tails that increase subgap absorption and recombination
 7 and degrades the CZTSSe solar cell open circuit voltage.^[9] Because
 8 process engineering appears to be difficult to manage defect gen-
 9 eration in stoichiometric CZTS, it has become common practice to
 10 use Cu-poor, Zn-rich CZTS as the absorber in high-performance
 11 CZTS solar cells.^[10,11] In addition, cationic substitution has been
 12 intensively studied in recent years to mitigate the cationic disorder
 13 phenomenon. The technique of cationic substitution is based on
 14 introducing an isovalent cation with a dissimilar ionic size to cat-
 15 ions in CZTS to increase the formation energy of antisite defects
 16 so that the amount of these defects can be reduced. Thus far, many
 17 cations (Bi, Cd, Ag, Cr) have been incorporated by various research
 18 groups into CZTS.^[12–15] For Cd, Su et al. reported a large increase
 19 in PCE of sol-gel spin-coated and sulfurized CZCTS/CdS devices
 20 from 5.3% to 9.24% at 40% substitution by Cd.^[16]
 21 The second limitation of CZTS is the thermal instability.
 22 Upon heating in N₂, CZTS can decompose into Cu₂S, ZnS,
 23 and SnS secondary phases.^[17] This necessitates the use of S-rich
 24 ambient in postdeposition annealing of polycrystalline CZTS.^[18]
 25 For device fabrication, CZTS is typically deposited on a Mo back
 26 contact layer. During sulfurization, sulfur can react with Mo to
 27 form MoS₂ as well as the secondary phases mentioned previ-
 28 ously. As MoS₂ is resistive ($\approx 830 \Omega\text{cm}$),^[19] various barrier mat-
 29 erials, such as ZnO, TiN, TiB₂, C, and Ag, have been investigated
 30 as an intermediate layer (IL) to mitigate MoS₂ formation.^[17,20–23]
 31 In a recent presentation,^[24] we reported that sputter-deposited
 32 CuO thin films can limit the sulfurization of Mo films deposited
 33 on soda lime glass (SLG) substrates. As an IL material, CuO is
 34 interesting because similarly to CZTS it is sustainable and
 35 nontoxic. The earth abundance per unit atom of raw element
 36 for CuO can be calculated to be 23.05%, which is comparable to
 37 Si (28.2%).^[1] Furthermore, CuO is a p-type semiconductor with a
 38 direct bandgap of $\approx 1.5 \text{ eV}$.^[25] CuO is also related to Cu₂O, which
 39 is one of the earliest photovoltaic materials that are still actively
 40 studied today.^[26] In this article, we investigate the impact of ultra-
 41 thin CuO IL on CZCTS absorber quality and the photovoltaic

performance of sol-gel-derived CZCTS/CdS thin film solar cells.
 By using an appropriate thickness of CuO, the incorporation of
 CuO IL can remarkably improve the CZCTS/Mo interface qual-
 ity, charge carrier collection, and photovoltaic performance.
 Finally, this unique interface engineering approach offers an
 alternative route to achieving high PCE in kesterite solar cells.

2. Results and Discussion

2.1. Material Characterization

X-ray photoelectron spectroscopy (XPS) was used to study the
 surface of the as-deposited 32 nm CuO film. As shown in
Figure 1a, peaks located at binding energies of 934 and 954.4 eV
 are ascribed to Cu 2p_{3/2} and Cu 2p_{1/2}.^[26,27] In addition, two
 strong Cu²⁺ satellite peaks at 943 and 962.5 eV are present, fur-
 ther confirming that Cu is present in the oxidation state of +2.
 Moreover, the presence of oxygen in the film was confirmed by
 the detection of a peak located at 531.1 eV which corresponds to
 the O 1s core shell^[28] (Figure 1b). Thus, it can be concluded that
 as-deposited IL is cupric oxide (CuO). Furthermore, the compo-
 sition at the surface of Mo/SLG samples without and with CuO
 ILs was characterized using XPS after peeling off the CZCTS
 absorber layer (Figure S1, Supporting Information). The study
 reveals peaks located at 229.1 and 232.2 eV attributed to Mo
 3d_{5/2} and Mo 3d_{3/2},^[29] respectively, as shown in Figure S1a,
 Supporting Information. Moreover, Figure S1b, Supporting
 Information, shows peaks at 161.9 and 163.1 eV, which are
 ascribed to S 2p_{3/2} and S 2p_{1/2}, respectively.^[29] This shows
 the formation of MoS₂ at the surface for the samples without
 and with CuO ILs. In addition, Figure S1c, Supporting
 Information, also demonstrates that after sulfurization Cu is
 present in the oxidation state of +1, whereas, XPS study of
 the as-deposited CuO reveals that the oxidation state of Cu is
 +2. This is due to the presence of peaks located at 931.9 and
 951.7 eV assigned to Cu 2p_{3/2} and Cu 2p_{1/2}, respectively.^[30]
 Thus, it is worth noting that the CuO ILs with thickness ranging
 from 4 to 32 nm are consumed as a result of the sulfurization.

Structural properties of the CZCTS thin films deposited on
 Mo-coated SLG (Mo-SLG) without and with a CuO IL after sul-
 furization were studied using X-ray diffraction (XRD) (**Figure 2**).

Figure 1. High-resolution XPS scan of a) Cu 2p and b) O 1s for as-deposited 32 nm thick CuO film.

Figure 2. XRD analysis of CZCTS/Mo thin films without and with a CuO IL.

to the A and E vibrational modes of CZCTS, respectively. The Raman shifts of these peaks are very similar to the reported values for CZTS. The A mode of CZTS (and CZTSe) represents the vibration of the chalcogen atom with the neighboring atoms stationary.^[31] According to the extended Keating theory,^[32] the frequency of the A mode of CZTS and CZTSe is given by $\nu = \sqrt{(2\alpha_{\text{Cu-VI}} + \alpha_{\text{Zn-VI}} + \alpha_{\text{Sn-VI}})/M_{\text{VI}}}$, where $\alpha_{\text{Cu-VI}}$, $\alpha_{\text{Zn-VI}}$, and $\alpha_{\text{Sn-VI}}$ are the bond-stretching force constants between the S(Se) atom and the respective metal atoms and M_{VI} is the relative atomic mass of S(Se). The bond-stretching force constants $\alpha_{\text{Y-VI}}$ are given by the equation: $\alpha_{\text{Y-VI}} = \alpha_1 d^{-x}$, where α_1 and x are constants and d is the bond length between the metal Y and S(Se). The shift of the main A peak to a lower wavenumber with respect to the reference sample for CuO 18 nm and CuO 32 nm samples is observed. There are two possible reasons for this. First, incorporation of a CuO IL at the back interface may affect the film stress in the CZCTS absorber layer and bond length of the nearest neighbor metal and S atoms. The second possible reason is the change in composition of the CZCTS thin film due to the incorporation of the CuO ILs. It has been shown in our earlier materials study^[24] that inclusion of a 10 nm CuO IL at the back interface caused modification of elemental diffusion profiles within the CZCTS layer. Furthermore, the laser penetration depth in CZTS is reported to be ≈ 100 nm.^[20] Therefore, the possible change in the Cd/Zn ratio in this case in the top 100 nm of the layers could also cause the shift of the Raman peak. Although the difference in the full width at half maximum (FWHM) of the main A vibrational peak for the control and CuO 4 nm samples is negligible, there is a marked increase of it for the CuO 18 nm and CuO 32 nm samples, respectively. This clearly signifies increased structural disorder of the CZCTS layer when a thick CuO IL is present at the interface between CZCTS and Mo.

The cross-section morphology of CZCTS thin film solar cells without and with CuO ILs was studied by field emission scanning electron microscopy (FESEM). Although an MoS₂ interfacial layer is barely seen for the control sample (Figure 4a), voids are present at the interface between the CZCTS absorber layer and Mo back electrode. Furthermore, the voids can also be observed between CZCTS crystallites at the bottom portion of the absorber layer. It is explained by the evaporation of volatile secondary phases which are the product of a solid-state reaction at the back interface between Mo and CZCTS.^[17] On the other hand, Figure 4b–d demonstrates that incorporation of CuO IL reduces voids at the interface and between CZCTS crystallites in the bottom part of the absorber layer. The observed effect is more pronounced for samples with 18 and 32 nm CuO ILs. This suggests that the CuO IL effectively mitigates the reaction at the back interface as the CuO IL thickness increases. The explanation for this effect is that the CuO IL eliminates direct contact between CZCTS and Mo.

Top surface morphology and roughness of CZCTS thin films with and without an 18 nm CuO IL was studied by atomic force microscopy (AFM), as shown in Figure S2, Supporting Information. The calculated surface roughness of the CZCTS thin film decreases slightly from 130.5 to 127.2 nm due to the incorporation of the 18 nm CuO IL. This demonstrates that deposition of the CuO IL does not lead to change in the surface roughness of the CZCTS absorber layer.

Figure 3. Raman spectroscopy characterization of CZCTS/Mo thin films without and with a CuO IL.

Figure 4. Cross-section SEM image of CZCTS solar cells of a) control device and with b) 4 nm CuO IL, c) 18 nm CuO IL, and d) 32 nm CuO IL.

2.2. Device Characterization

The current density–voltage (J – V) characteristics of the CZCTS solar cells under illumination without and with a CuO IL were recorded to study the effect of CuO IL thickness on the photovoltaic properties of the devices. The light J – V curves, measured under the standard illumination conditions of 1 sun, AM 1.5G, are shown in **Figure 5a**. The photovoltaic parameters extracted from the J – V characteristics of the solar cells are given in **Table 1**. For each CuO IL thickness and the reference, ten devices were tested. The parameters of the device with maximum PCE from each batch of devices (reference, CuO 4 nm, CuO 18 nm, and CuO 32 nm) are highlighted together with the batch average and standard deviation. As shown in Table 1, the best reference CZCTS/CdS device exhibits an open-circuit voltage (V_{oc}) of 613 mV, short-circuit current density (J_{sc}) of 25.28 mA cm^{-2} , and fill factor (FF) of 64.69% resulting in a PCE of 10.03%. On the other hand, the CZCTS/CdS solar cell with a 4 nm CuO IL demonstrates improvement in photovoltaic performance and attains a maximum PCE of 10.77%. The enhancement of the device performance is mostly associated with a boost in J_{sc} by 7% from 25.28 to 27.11 mA cm^{-2} , whereas the change in both the V_{oc} and FF is quite negligible. J_{sc} is further increased to its maximum value of 28.46 mA cm^{-2} when an 18 nm of CuO IL is present at the Mo back interface. Note that the device with the highest PCE in a batch may not have the highest J_{sc} . Thus, the CuO 18 nm device shows an $\approx 13\%$ increment in J_{sc} compared to the reference solar cell. However, deposition of an 18 nm CuO IL results in decrease of the PCE to 10.38% as the V_{oc} and FF drop to 592.3 mV and 61.59%, respectively. Further increase of CuO IL thickness up to 32 nm leads not only to a lower V_{oc} and FF of 561.5 mV and 58.7%, respectively, but

also to a slight decrease of J_{sc} . This results in a significant drop of PCE to 9.25%.

As J_{sc} is the main reason for the PCE improvement, external quantum efficiency (EQE) spectra were measured to study the impact of CuO IL thickness on spectral response and carrier collection of the CZCTS solar cells. Figure 5b shows that the recorded EQE spectra correlate with measured J_{sc} for the analyzed solar cells. In addition, it has been found that the absorption edge shifts slightly to the longer wavelength with the increase of CuO thickness. It can be attributed to the reduction of the CZCTS bandgap from 1.39 to 1.37 eV when the thickness of the CuO IL increases from 0 to 32 nm (**Table 2**). The method of bandgap extraction is based on the first derivative of the EQE with respect to photon energy (Figure 5d). With the increase of CuO IL thickness, there is slight variation in the Zn and Cd composition.^[24] This may be responsible for the decrease in the optical bandgap of CZCTS.

Figure 5c shows normalized EQE spectra for the solar cells without and with CuO ILs of different thicknesses. The plot with normalized EQE data helps to identify the wavelength regions with modified charge carrier collection as a result of CuO IL incorporation. The measured data reveal that charge carrier collection in the wavelength range from 550 to 900 nm improves steadily with CuO incorporation until the IL reaches the thickness of 18 nm. This may be due to fewer voids and better back interface quality, as the CuO IL is inserted. For the CuO 32 nm sample, however, there is a distinct degradation of the carrier collection in the aforementioned wavelength range. Moreover, insertion of the CuO IL at the back interface causes change in spectral response in the range from 380 to 530 nm. This spectral range is associated with the absorption by the CdS buffer layer. Nevertheless, improvement in overall charge carrier collection

Figure 5. a) Light and dark J - V characteristics, b) EQE spectra, c) normalized EQE spectra, and d) plot of first derivative of EQE versus photon energy for CZCTS solar cells without and with a CuO IL.

Table 1. Summarized photovoltaic parameters of CZCTS solar cells without and with a CuO IL (average value and standard deviation of the measured parameters are mentioned in parentheses) and calculated depletion width.

	V_{oc} [mV]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]	Depletion width [nm]
Ref.	613 (609.1 ± 11.1)	25.28 (25.21 ± 0.29)	64.69 (59 ± 4.9)	10.03 (9.07 ± 0.87)	60
CuO 4 nm	615.7 (606.6 ± 10)	27.11 (26.57 ± 0.6)	64.52 (58.48 ± 5.38)	10.77 (9.42 ± 0.91)	87
CuO 18 nm	592.3 (597.2 ± 17.5)	28.46 (28.16 ± 0.68)	61.59 (55.81 ± 3.62)	10.38 (9.39 ± 0.67)	105
CuO 32 nm	561.5 (564.6 ± 24.5)	28.05 (28.22 ± 1.18)	58.7 (55.6 ± 2.8)	9.25 (8.84 ± 0.27)	125

Table 2. Bandgap of the absorber layers extracted from EQE spectra.

	Ref.	CuO 4 nm	CuO 18 nm	CuO 32 nm
Bandgap, eV	1.39	1.39	1.38	1.37

1 is more significant than due to improvement in the two wave-
2 length ranges (Figure 5b). Reduced density of defects at the
3 CZCTS/CdS interface causing better overall charge carrier collec-
4 tion can be a possible reason for the observed improvement in
5 overall EQE.^[3]

6 The effect of the CuO IL thickness on the space charge region
7 of CZCTS was investigated by capacitance-voltage (C - V) dopant

profiling. The analysis shows a drop of apparent charge density 1
 N_{cv} and increase of depletion width when the thickness of the 2
CuO IL is increased (Figure 6a). The calculated depletion width 3
(for an ac amplitude of 30 mV at 10 KHz) for the control samples 4
is 60 nm, whereas it increases to 87, 105, and 125 nm for the 5
CuO 4 nm, CuO 18 nm, and CuO 32 nm samples, respectively. 6
A possible explanation for the effect is the modification of the Cu 7
diffusion profile due to the presence of CuO ILs. Cu-based IL 8
mitigates diffusion of elemental Cu in Mo^[24] and, therefore, 9
may reduce the density of copper vacancies (V_{Cu}) within the 10
CZCTS absorber layer. Because V_{Cu} forms a shallow acceptor 11
level in CZTS,^[33] the density of these defects may be crucial 12
for the majority carrier density in p-type CZCTS. Thus, 13

Figure 6. C-V characterization of CZCTS solar cells without and with a CuO IL. a) Estimation of depletion width and b) extraction of built-in voltage.

1 improvement in overall charge carrier collection can be associ-
2 ated with the increase of depletion width. Moreover, Figure 6b
3 shows that the trend in built-in voltage (V_{bi}) correlates with
4 the trend in V_{oc} .

5 In the literature, the performance of the photovoltaic devices
6 reported are typically those measured at the time of fabrication
7 and the change in PCE over time is seldom studied. However, for
8 device upscaling and energy conversion application, the behavior
9 of the device over time is critical and high PCE is much sought
10 after. The light $J-V$ characteristics of CZCTS/CdS solar cells
11 without and with a CuO IL under varying illumination intensity
12 (0.125–2.3 sun) were measured 124 days after device fabrication
13 (Figure 7a,c,e,g). The devices were stored in the dark in a
14 humidity-controlled laboratory dry box. For all devices in this
15 series, there is an increase in V_{oc} and J_{sc} with illumination
16 intensity (Figure 7b,d,f,h). The value of V_{oc} increases from less
17 than 500 mV for the lowest illumination intensity and then
18 approaches an asymptotic value. On the other hand, J_{sc} increases
19 linearly with illumination intensity. This intensity dependence
20 can be explained by the increased concentration of photogener-
21 ated carriers and the accompanying shifts of the quasi-Fermi
22 levels of the absorber and the buffer layer. The FF of the refer-
23 ence device increases from $\approx 35\%$ at 0.125 sun toward a limiting
24 value at higher intensities. For the CuO 4 nm and CuO 18 nm
25 devices, the FF increases initially toward a maximum near
26 0.5 sun and then decreases. This is different from CuO 32 nm,
27 for which the FF decreases monotonically from an initial maxi-
28 mum at $\approx 65\%$. It is also evident that the observed reduction in
29 the FF and V_{oc} of the solar cells at low illumination intensity
30 (0.125–0.5 sun) is diminished with an increase of CuO IL thick-
31 ness. In other words, the FF at low illumination intensity is
32 higher for devices with a thicker CuO IL. This may be explained
33 by the reduced recombination loss and improved carrier
34 collection compared with the reference device.^[7] However, for
35 all devices with a CuO IL, the FF decreases with illumination
36 intensity for intensity above 0.5 sun.

37 **Figure 8** shows the device PCE as a function of illumination
38 intensity for the best devices with and without a CuO IL at
39 124 days after fabrication. **Table 3** shows the photovoltaic
40 parameters of these devices measured at an irradiance of 1 sun.

1 In addition, **Table 4** summarizes published results on aging of
2 kesterite solar cells. The PCE of the reference device in Figure 8
3 increases with illumination intensity and approaches a limiting
4 value of 7% at 2.3 sun. In particular, the PCE of the reference
5 device under 1 sun illumination drops from 10% to 7.06%.
6 The device performance is mostly degraded due to the decrease
7 in FF from 64.69% to 53.1% and V_{oc} from 613 to 543 mV.
8 However, the change in short-circuit current density is less sig-
9 nificant than that of FF and V_{oc} , with J_{sc} reducing from 25.28 to
10 24.49 mA cm^{-2} . On the other hand, Figure 8 reveals that with the
11 increase of CuO IL thickness, the CZCTS solar cells exhibit pro-
12 gressively smaller decrease in the magnitude of PCE with storage
13 time at 1 sun. This can be seen more clearly from the ΔPCE
14 column in Table 3, where ΔPCE is defined as the difference
15 between the PCE at 124 days and the initial PCE of the device.
16 For CuO 4 nm and CuO 18 nm, the decrease is mainly due to
17 decrease in V_{oc} and FF, similar to the reference device. The
18 change in J_{sc} is relatively small. Interestingly, the CuO 32 nm
19 solar cell shows an unexpected increase of PCE from 9.25% to
20 9.88% as a result of the aging. In fact, CuO 32 nm is the only
21 device that does not show a decrease in FF and it has the smallest
22 V_{oc} drop from 561.5 to 529 mV over 124 days. Although addi-
23 tional device characterization will need to be conducted, this
24 observation strongly suggests that the PCE stability of the devices
25 is influenced by the CuO IL thickness. As the CZCTS/CdS inter-
26 face and thickness of CZTS are identical for all the devices,
27 the improvement of stability of the device can be associated with
28 the back interface modification.

29 Residual stress at the back interface due to the high-
30 temperature sulfurization was claimed to be a reason for poor
31 absorber layer adhesion.^[34] It also has been reported that
32 degradation of CZTS solar cell photovoltaic properties may be
33 attributed to the adhesion failures at the interface between the
34 Mo back contact and the CZTS absorber layer.^[34] In addition,
35 Raman spectroscopy analysis of CZCTS thin films reveals a
36 change in the residual stress with the increase of CuO IL thick-
37 ness. Therefore, a possible explanation for the significantly
38 improved stability of the CZCTS solar cells is accommodation
39 of the residual stress at the back interface by incorporation of
40 the CuO IL. Although there are other possible factors apart from

Figure 7. Light J - V characteristics and photovoltaic parameters measured under various illumination intensities of a,b) control device, c,d) CuO 4 nm, e,f) CuO 18 nm, and g,h) CuO 32 nm solar cells. The measurements were conducted 124 days after the fabrication of the devices.

Figure 8. PCE of CZCTS solar cells measured under various illuminations 124 days after device fabrication.

Table 3. Photovoltaic parameters of the best CZCTS solar cells without and with a CuO IL measured 124 days after fabrication at an illumination of 1 sun.

	V_{oc} [mV]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]	ΔPCE [%]
Ref.	542.8	24.49	53.1	7.06	-2.97
CuO 4 nm	552.1	26.11	54.6	7.87	-2.90
CuO 18 nm	545.7	28.36	56.13	8.69	-1.69
CuO 32 nm	528.9	31.42	59.49	9.88	+0.63

1 the back contact properties that can contribute to CZTS
2 degradation and further investigation is required to reveal the
3 exact mechanism of stability improvement for the devices
4 with a CuO IL, we noted that the presence of the CuO IL enables
5 suppression of the back interface reaction between Mo and
6 S during thermal treatment. Both the thickness and composition
7 of the IL are very critical toward the performance of the
8 devices.^[11,24]

Table 4. Reported results of stability tests for kesterite solar cells.

Absorber layer	Precursor deposition approach	Aging conditions	IL (if any)	PCE modification	Ref.
CZTS	Co-sputtering	225 days in open air	NA	Decreased from 10.81% to 9.85%	[35]
CZTSSe	Spin coating	55 days in dry box in low N_2 flow	20 nm MoO_3	Increased from 10.9% to 11% (exfoliated solar cell with Au back contact)	[36]
CZTSe	Sequential sputtering	>41 days at 85 °C and humidity of 85%	NA	Mo back contact: decreased from 3.97% to 1.19%; FTO back contact: decreased from 3.21% to 1.61%	[37]
CZTS	Monograins	$\approx$ 4 days at 105 °C in dry air	NA	Decreased from 5.44% to 3.67%	[38]
CZTSSe	Monograins	$\approx$ 4 days at 105 °C in dry air	NA	Decreased from 6.08% to 3.98%	[38]
CZCTS	Spin coating	124 days in dry box in air	NA	Decreased from 10.03% to 7.06%	This study
CZCTS	Spin-coating	124 days in dry box in air	4 nm CuO	Decreased from 10.77% to 7.87%	This study
CZCTS	Spin coating	124 days in dry box in air	18 nm CuO	Decreased from 10.38% to 8.69%	This study
CZCTS	Spin coating	124 days in dry box in air	32 nm CuO	Increased from 9.25% to 9.88%	This study

3. Conclusion

Insertion of a nanoscale CuO IL at the CZCTS/Mo interface has a significant impact on device performance and stability. The effect of CuO IL thickness on photovoltaic properties of CZCTS/CdS solar cells includes improvement in the collection of photogenerated carriers, depletion width, and photocurrent. Incorporation of a 4 nm thick CuO IL results in improvement of device performance from 10% to 10.8% due to increase in J_{sc} . The device with an 18 nm CuO IL shows remarkable enhancement of the J_{sc} . However, a thicker layer of CuO IL slightly reduces the V_{oc} and FF. The CuO IL thickness has a significant impact on the stability of the devices. After a storage period of 124 days, the rate of PCE decrease is found to improve from the value of -0.58% per month for devices without CuO to -0.38% per month for the device with CuO thickness of 18 nm. For the device with CuO thickness of 32 nm, there is a gain in PCE at the rate of $+0.126\%$ per month. This work opens up the opportunity to design pure sulfide-based stable solar cells with high efficiency.

4. Experimental Section

Device Fabrication: Mo-SLG substrates were ultrasonically cleaned in soap water, acetone, ethanol, and deionized water (DIW), followed by drying in N_2 flow. This was followed by CuO IL sputter deposition in a Denton Discovery 18 magnetron sputtering system. The sputtering chamber evacuated by a turbomolecular pump had a base pressure of 8×10^{-5} Pa. During sputtering using Ar plasma, a working pressure of 0.48 Pa was typically used. For the CuO IL deposition, a radio frequency (RF) sputtering power of 100 W was applied to a 99.99% purity CuO target (ALB Materials Inc.) to deposit 4, 18, and 32 nm thick CuO films on Mo-SLG substrates. These samples were labelled as CuO 4 nm, CuO 18 nm, and CuO 32 nm, respectively.

The absorber layer was prepared by a sol-gel spin-coating and sulfurization process. The precursor solution for the CZCTS thin film deposition was prepared by dissolving copper acetate monohydrate (0.38 mol L^{-1}), zinc acetate dihydrate (0.15 mol L^{-1}), cadmium acetate dihydrate (0.1 mol L^{-1}), tin chloride dihydrate (0.2 mol L^{-1}), and thiourea (1.6 mol L^{-1}) in 2-methoxyethanol under continuous stirring for 2 h at 50 °C. A few drops of monoethylamine and trimethylamine stabilizers were then added into the solution. The Cd/(Zn + Cd) concentration ratio in the precursor solution was adjusted to the previously optimized value of 0.4.^[16] Thereafter, the solution was spin-coated over the substrates at

1 4000 RPM for 20 s, followed by annealing in air at 280 °C for 2 min. After
 2 this “deposition-annealing” process had been repeated 14 times, the sam-
 3 ples were sulfurized in a mixed atmosphere of elemental sulfur (S) and
 4 argon (Ar) at 600 °C for 40 min in a two-zone tube furnace, resulting in
 5 the formation of a 1 µm thick CZCTS absorber layer. This was followed
 6 by chemical bath deposition (CBD) of a 60 nm CdS buffer layer. The
 7 CBD precursor solution consisted of a mixture of 140 mL distilled water,
 8 20 mL aqueous solution of CdSO₄ (0.015 M), 23 mL of 28–30% aqueous
 9 NH₄OH solution, and 20 mL aqueous thiourea solution (0.75 M). The CBD
 10 process was conducted at 80 °C for 9 min under continuous stirring. An RF
 11 sputtering power of 50 W was used for the deposition of a 40 nm thick
 12 ZnO window layer and 300 nm thick indium tin oxide (ITO) layer. To
 13 reduce lattice damage to the CdS buffer layer during ZnO deposition,
 14 the RF sputtering power was increased slowly. The samples were
 15 subjected to a final anneal in an Ar atmosphere at 300 °C for 10 min.
 16 Finally, mechanical scribing was used to define individual cells, while
 17 Ag paste was printed to make contacts. The active area of the solar cells
 18 was ≈0.15 cm².

19 **Thin Film Characterization:** The structural properties of the CZCTS thin
 20 films were studied by XRD analysis using a Bruker D8 diffractometer with a
 21 Cu Kα source wavelength of 0.15418 nm. Supplementary structural char-
 22 acterization was performed using a Raman spectrometer equipped with a
 23 488 nm laser. After peeling off the CZCTS absorber layer by adhesive tape,
 24 the surface of the Mo/SLG samples with and without a CuO IL was
 25 analyzed by XPS spectroscopy using a VG ESCALAB 220i-XL spectrometer
 26 with a monochromatic Al Kα source (1486.6 eV). Charge collection refer-
 27 ence was performed using the C 1s peak at 284.6 eV. Au, Ag, and Cu poly-
 28 crystalline foils were used for calibrating the electron analyzer of the XPS
 29 system. The cross-section morphology of the samples was investigated by
 30 using FESEM (JEOL FESEM JSM 7600F). Atomic force microscopy (AFM)
 31 was performed using an Asylum Research MFP-3D with Pt–Ir-coated
 32 conducting silicon probes (PPP-EFM, Nanosensors) with a nominal force
 33 constant of 2.8 N m^{−1} used for this measurement.

34 **Solar Cell Characterization:** A Keithley 2612A source meter and VS-0852
 35 solar simulator based on a Xe-lamp source were used to measure light J–V
 36 characteristics under air mass AM 1.5 global spectrum and standard light
 37 intensity of 100 mW cm^{−2} (1 sun). Prior to the measurement, the solar
 38 simulator was calibrated with a certified Si reference solar cell. For
 39 intensity-dependent J–V measurements, the illumination intensity was
 40 varied in the range of 0.125–2.3 sun. A Bentham PVE 300 system, cali-
 41 brated using a reference Si photodetector, was implemented to record
 42 the EQE spectra of the solar cells. C–V measurements were conducted
 43 using a Metrohm Autolab PGSTAT302N system.

44 Supporting Information

45 Supporting Information is available from the Wiley Online Library or from
 46 the author.

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51 Conflict of Interest

52 The authors declare no conflict of interest.

53 Keywords

54 CuO intermediate layer, Cu₂(Zn_{0.6}Cd_{0.4})SnS₄, interface engineering,
 55 kesterite solar cells, stability

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