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1 **Suppressing Surface and Bulk Effect enables High Efficiency**
2 **Solution-Processed Kesterite Solar Cells**

3

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15

16 **Abstract**

17 Kesterite $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) is a promising photovoltaic material due to its
18 environmentally friendly composition and excellent photovoltaic performance.
19 Unfortunately, open-circuit voltage (V_{oc}) deficit and insufficient fill factor (FF) due to
20 the interface and bulk carrier recombination have become major obstacle to further
21 improve the device performance. A new effective strategy is proposed to
22 simultaneously improve the front interface and suppress the CZTSSe absorber defects
23 by introducing a thin ammonium sulfide layer on the absorber surface by a pre-soaking
24 and spin-coating-annealing method. Through this strategy, the absorber surface is
25 optimized by adding S and removing the secondary phase. At the same time, the
26 diffusion of S into the bulk transforms the dominant deep V_{Se} defect into shallower
27 Cu_{Zn} defect, which effectively reduces carrier recombination in the CZTSSe bulk and
28 at the CZTSSe/CdS interface, prolongs minority carrier lifetime, facilitates carrier
29 collection, and reduces charge loss. The optimized sulfurization treatment significantly
30 improves V_{oc} and FF to the point that device efficiency increases from 11.26% to
31 13.19%. These findings provide new insights into achieving higher efficiency in
32 CZTSSe-based thin film solar cells by simultaneously optimizing the interface and bulk.

33 **Keywords:**

34 CZTSSe, solar cell, surface sulfurization, carrier transport enhancement, defects
35 passivation

36

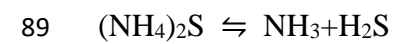
37 **Introduction**

38 The Earth's abundant reserves of kesterite $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) thin film has
39 attracted extensive research interest in the last decade for the green non-toxicity and
40 high-efficiency solar cells due to the high light absorption coefficient, tunable direct
41 bandgap (E_g) and high quantum efficiency[1, 2]. However, as the most promising
42 alternative to $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ (CIGS) solar cells, the power conversion efficiency (PCE)
43 of CZTSSe (14.9%) is still far below the highest performance of CIGS solar cells
44 (23.6%)[3]. Among the many factors constraining the improvement of device efficiency,
45 carrier recombination at the heterojunction interface and the absorber bulk should be
46 the key limiting factor. Interface and bulk defects leads to increased Shockley-Reed-
47 Hall recombination (i.e., trap-assisted recombination), which inevitably results in larger
48 open-circuit voltage deficit ($V_{\text{OC-def}}$)[4]. Meanwhile, a series of secondary phases are
49 inevitably generated during the selenization process, which affects the attachment
50 between the buffer layer and absorber and reduce the filling factor (FF)[5, 6]. Besides,
51 the $\text{Sn}(\text{S},\text{Se})$ is commonly used to suppress Sn loss at selenization progress, excess
52 $\text{Sn}(\text{S},\text{Se})$ may condense on absorber surface when it was cooling[7, 8]. The deep level
53 defects in the absorber can be effectively passivated by cation (Ag, Cd, Ge, et al.)
54 doping, and changing the selenization process to control the chemical environment
55 during the crystallization process can also obtain absorber with lower defect density[9-
56 11]. However, it is very difficult to improve the absorber bulk as well as the
57 heterojunction interface properties by one strategy at the same time. It is necessary to
58 find a way to solve both the defect and the interface problem to further increase the V_{OC}
59 and FF. Electroactive defect reduction and secondary phase elimination at the

60 CZTSSe/CdS interface by surface treatment is an effective way to improve the quality
61 of the heterojunction interface[6, 12].

62 Among the various guiding interface treatment strategy, sulfurization of the CZTSSe
63 absorber has proven to be a simple and effective method[13, 14]. It consists of two main
64 approaches: sulfur-containing vapor treatment and solution treatment. Post-annealing
65 treatment at elevated temperatures under H₂S gas or S vapor atmosphere can effectively
66 increase the V_{OC} , and the increase is usually attributed to the activation energy transfer
67 of the interface state at the CZTSSe/CdS interface[15, 16]. In this case, the electron
68 transport barrier formed on the surface of the S-rich component deteriorates the device
69 efficiency, so it is essential to control the additional sulfur content introduced by the
70 sulfurization treatment[17]. However, it is very difficult to accurately regulate sulfur
71 doping in CZTSSe film during sulfurization treatment because of the high activity of
72 sulfur at high temperature. Besides, due to the decomposition of kesterite film at high
73 temperatures, elements such as Sn are easily lost. Sulfur-containing solution soaking,
74 such as (NH₄)₂S and Na₂S treatments could take out the secondary phase on the
75 absorber surface and improve the surface wettability of absorber[7, 18]. However, the
76 appropriate treatment time is crucial for the solution sulfurization treatment, and the
77 absorber needs to be washed immediately after the treatment. The sulfurization activity
78 is closely related to the reaction temperature, which makes it difficult to achieve the
79 passivation of defects by this method. In order to achieve an effective sulfurization
80 effect and at the same time a good control of the degree of sulfurization, a new
81 sulfurization process needs to be explored.

82 In the present contribution, we report on an effective and simple solution treatment
83 method that can be applied on the surface of sulfur-based thin films and achieve vapor
84 sulfurization, being able to adjust simultaneously the surface property as well as the
85 internal defect of the absorber. This method is based on the use of vapor from
86 ammonium sulphide ((NH₄)₂S, abbreviated here AS) as a sulfur source. AS is a salt of
87 a weak alkali and a weak acid and thermally decomposes at 280 °C to release H₂S as
88 follows[19, 20],



90 compare with the solution soaking sulfurization process alone, the H₂S released at
91 280 °C is expected to obtain higher reactivity, while the benign treatment temperature
92 of 280 °C promotes the diffusion of S elements, which can effectively passivate the
93 interface defects as well as bulk defects. Therefore, AS sulfurization treatment is
94 expected to suppress interface and bulk recombination synergistically and well control
95 the elemental distribution, thus further improving the heterojunction quality and device
96 performance.

97 Here, we provide an effective surface sulfurization method to optimize CZTSSe surface
98 and passivate interface and bulk defect. The AS solution was coated on the CZTSSe
99 absorber and stayed for 2 min, then spinning was performed to obtain thin AS layer on
100 the absorber surface, finally sintered at 280 °C under inert atmosphere. The synergistic
101 effect of surface etching and surface sulfurization can be obtained simultaneously by
102 this method. After the surface sulfurization treatment, the sulfur content of absorber
103 was slightly increased, carrier separation efficiency was enhanced and the carrier

104 recombination was suppressed. This combined factors of enhanced charge transport
105 capacity, reduced carrier recombination and extended carrier lifetime resulted in a
106 significant increase in V_{OC} and FF and a device efficiency of 13.19% (the total-area
107 efficiency is 12.71%).

108

109 **Experiment**

110 Preparation of CZTS precursor solution: The molar ratio of Cu/(Zn+Sn) and Zn/Sn
111 were 0.775 and 1.2, respectively, and the solutions were prepared in air. Sn^{4+} solution
112 was obtained by dissolving CuCl, $Zn(CH_3COO)_2 \cdot 2H_2O$, $SnCl_4 \cdot 5H_2O$ and $SC(NH_2)_2$ in
113 2-Methoxyethanol. Sn^{2+} solution was prepared by dissolving $Cu(CH_3COO)_2 \cdot H_2O$,
114 $ZnCl_2$, $SnCl_2 \cdot 2H_2O$ and $SC(NH_2)_2$ in 2-Methoxyethanol. The Sn^{4+} and Sn^{2+} solution
115 were mixed homogeneously in the same volume and then diluted to half of the original
116 concentration to obtain the CZTS precursor solution.

117 Preparation of CZTSSe absorber: The CZTS precursor solution was spin-coated Mo
118 substrate. The rotational speed was 3000 rpm and the film was annealed in a hot plate
119 at 280 °C after spin-coating. This spin-coating and annealing cycle was repeated 10
120 times. Finally, the prepared CZTS precursor film were seleniated in a rapid thermal
121 processing (RTP) furnace at 555 °C, 900 s, and under argon flow to obtain CZTSSe
122 absorber.

123 Sulfurization treatment: Method A: Soak the CZTSSe absorber in ammonium sulphide
124 solution, use a stopwatch to accurately calculate the soaking time, and rinse the film
125 with deionised water immediately after the soaking. The rinsed film was dried in an

126 oven at 60 °C. Method B: Place the CZTSSe absorber in the spin coater machine and
127 use a dropper to draw ammonium sulphide solution onto the absorber surface so that
128 the surface is completely covered by the ammonium sulphide solution. The infiltration
129 time was accurately calculated using a stopwatch, and the spin coater machine was
130 started immediately after the timing to rotate the film. The CZTSSe absorber covered
131 with AS layer were then annealed on a hot plate at 280 °C. The same spin-coating
132 parameters were used for the CTZS film and the AS layer. The solution was spin-coated
133 with 3000 rpm for 20 s. The whole process was carried out in a glove box under nitrogen
134 atmosphere.

135 Device preparation: The CdS buffer layer was prepared by chemical bath deposition on
136 absorber. The ITO window layer was sputtered by magnetron sputtering on the buffer
137 layer. Ag electrodes were deposited by thermal evaporation.

138 Characterizations: The X-ray diffraction (XRD) pattern was measured by Bruker AXS
139 (D8 Advance). The surface topography and Mapping of the films were obtained using
140 scanning electron microscopy (BRUKER QUANTAX 200). The current density-
141 voltage (*J-V*) characteristics were represented by a Keithley 2400 multi-meter. The
142 external quantum efficiency (EQE) spectrum were collected by Zolix SCS101 system
143 and Keithley 2400 source meter. Ultraviolet photoelectron spectroscopy (UPS) were
144 obtained by PHI 5000 VersaProbe III with He I source (21.22 eV). The X-ray
145 photoelectron spectroscopy (XPS) was measured by PHI 5000 VersaProbe III with a
146 monochromatic Al K α X-ray source. The topography and surface potential were
147 measured by Kelvin Electrostatic Force Microscopy (KPFM, Dimension Icon, Bruker).

148 Electrochemistry impedance spectroscopy (EIS) was measured by frequency response
149 analysis (FRA) equipped PGSTAT-30 from Autolab (AUT302N). Temperature-
150 dependent dark $J-V$ ($J-V-T$) measurement were carried out using a Lakeshore 325
151 temperature controller. The transient photovoltage (TPV) spectra were collected by
152 Agilent B1500A semiconductor characterization system. Admittance spectral
153 measurement was collected through Lakeshore 325 temperature controller and the
154 devices were mounted inside a Janis VPF-100 cryostat and the system was cooled with
155 liquid nitrogen. Capacitance-voltage (CV) and drive-level capacitance spectroscopy
156 (DLCP) were analysed by Keithley 4200A-SCS system with JANIS cryogenic platform.
157 The device was put into a SEM vacuum chamber to implement EBIC measurements
158 (Gatan, Inc.).

159

160 **Results and Discussion.**

161 **Figure 1a** demonstrates the preparation of CZTSSe thin films treated by AS solution
162 sulfurization. The conventional AS solution sulfurization method usually selects a
163 suitable soaking time to soak the CZTSSe absorber in AS solution at room temperature,
164 and then the film are placed in deionized water, and finally dried it to obtain the treated
165 film. The film prepared by the traditional method is called as sample A. The soaking
166 time of AS solution corresponding to sample A1 and A2 is 1 and 2 min, respectively.
167 Such a treatment removes secondary phase and passivates the defect of the absorber
168 surface to some extent. Overall, this method is convenient but cannot improve the
169 internal property (e.g., bulk defect) of the absorber, and thus the improvement of PCE

170 is limited. Therefore, we chose a new treatment method: firstly, drop the AS solution
171 on the CZTSSe absorber surface, so that the AS solution completely covers the whole
172 film surface, stay for a few minutes to remove the secondary phase of the surface. Then
173 turn on the spin coater machine, high-speed rotation makes the AS solution transformed
174 into a thin AS layer[6, 21, 22]. Finally the sample are placed on a hot plate at 280 °C
175 for annealing, the whole process was carried out in a glove box. The samples prepared
176 using this method are called sample B, and the AS solution infiltration time of sample
177 B1, B2 and B3 correspond to 1, 2 and 3 min, respectively. The H₂S released from the
178 decomposition of AS at 280 °C has higher reactivity, and the favorable sulfurization
179 temperature of 280 °C is conducive to promoting the diffusion of S into the interior of
180 the absorber, which can effectively passivate the defect on the surface as well as in the
181 bulk.

182 The XRD spectra and partial magnification of the reference sample and samples A, B
183 are shown in Figure 1b and c, respectively. The XRD spectra indicate that the crystal
184 structure of the samples is kesterite CZTSSe, and the bulge located on the right side of
185 the (112) peak is assigned to the secondary phase Sn(S, Se)[7, 23]. The Sn(S, Se) peak
186 intensity of the thin film treated with AS solution was significantly weakened than
187 reference (Figure 1c), indicating that the secondary phase in the absorber was
188 effectively removed. Moreover, the Sn(S,Se) peak intensity of A2 sample is lower than
189 that of A1, and the Sn(S,Se) peak intensity of B1, B2 and B3 are weakened in turn,
190 which means that the longer the AS solution stays on the absorber, the better the remove
191 effect of the secondary phase is.

192 To investigate the effect of AS solution treatment on the device efficiency, the PCE of
193 the reference sample and sample A, B are demonstrated in **Table 1**. The results show a
194 negligible slight enhancement in short-circuit current density (J_{SC}) and V_{OC} and a small
195 increase in FF, hence a slight enhancement in efficiency for the sample treated by
196 method A. AS solution soaking removes the secondary phase of absorber surface,
197 which favors better heterojunction quality, and therefore the FF is enhanced. The
198 increase in V_{OC} and FF in the samples treated with method B was quite significant.
199 Residence of the AS solution on the surface of the absorber dissolves the secondary
200 phase, and subsequent rotation of the spin coater machine removes the secondary phase
201 dissolved in the AS solution. Annealing at 280 °C in an inert gas atmosphere enhances
202 the reactivity of the sulfurization and promotes elemental diffusion, and the AS
203 decomposes into NH_3 and H_2S , which effectively passivates the electroactive defects
204 on the surface and in the bulk of the absorber. The improvement of the heterojunction
205 quality and the reduction of the defect lead to the enhancement of the FF and the V_{OC} ,
206 which resulted in an efficiency of 13.19%. The 2 minutes residence time of AS solution
207 gives the best result.

208 In the following, the reference device and the optimal device B2 will be referred to as
209 W/O AS and With AS respectively for ease of expression. **Figure 2a** illustrates the box
210 statistics of the PV parameters, where the average efficiency of the With AS device
211 increases from 11.15% to 12.76%. The enhancement of J_{SC} may originate from the
212 reduction of recombination loss at the heterojunction interface and the enhancement of
213 charge carrier collection[24]. SEM mapping test were performed on the surface of W/O

214 AS and With AS absorber to investigate the effect of AS treatment on the elemental
215 content of the absorber surface, and the result is displayed in Figure 2b, c. The S content
216 of With AS absorber surface increases obviously, the Se content changes insignificantly,
217 and the Sn content decreases slightly, which coincides with the result that the Sn-related
218 secondary phases are removed after the sulfurization treatment.

219 The EDS elemental line scan shows a slight increase of S content in the near-surface
220 region (400 nm) of the absorber after sulfurization treatment (**Figure 3a**). Figure 3b
221 demonstrates the changes of S/Se in the films before and after the sulfurization
222 treatment and the corresponding bandgap changes, and the calculation of the bandgap
223 based on S/Se is shown in the Supporting Information (**Note1**). With AS films
224 possessing a larger value of S/Se near the surface, the surface bandgap is larger than
225 that of the W/O AS films. The V_{OC} is proportional to the bandgap, and a slightly larger
226 bandgap at the surface favors the enhancement of the V_{OC} . XPS is very sensitive to the
227 elemental component of the sample surface, and the surface composition of the W/O
228 AS and With AS CZTSSe absorber was investigated using XPS. Figure 3c illustrates
229 the S 2p peak of both sample. Four peaks were observed in the S 2p spectra, the peaks
230 at 161.0 and 162.2 eV belonged to the S 2p core, consistent with the sulphide state S
231 located at 160-164 eV, while the peak at 159.7 and 165.4 eV belonged to the Se 3p
232 core[25, 26]. The sulfurization treatment greatly affects the surface S peak intensity, the
233 S peak intensity of the treated film surface is significantly increased compared to W/O
234 AS film, which implied that the surface of the treated film had a higher S content. It is
235 in agreement with the results of SEM-Mapping. Figure 3d shows the J-V curves of the

236 W/O AS and With AS device. The V_{OC} and FF of the With AS device demonstrates a
237 significant enhancement, which may originate from the passivation of defects and the
238 enhancement of bandgap. **Figure S1** shows the J-V curves for the light and dark states
239 of the W/O AS and With AS device, and the series resistance (R_s), shunt resistance (R_{sh}),
240 ideality factor (A), and reverse saturation current (J_0) calculated from the J-V curves
241 are summarized in **Table 2**[27, 28]. The diode parameters (**Figure S2** and **Figure S3**)
242 of the solar cell help us to analyze the performance loss mechanism of the device. With
243 AS device have smaller R_s and larger R_{sh} , which is beneficial to enhance the FF. The A
244 and J_0 of With AS devices are 1.5 and 1.57×10^{-5} mA cm⁻², respectively, which are
245 smaller than that of the W/O AS devices[29, 30]. It implies that there is a significant
246 reduction of carrier recombination in the With AS devices, which could be due to the
247 sulfurization treatment passivation defects thereby reducing the number of carrier
248 recombination centers.

249 The EQE curve are shown in Figure 3e. Consistent with J_{SC} , the AS sulfurization
250 treatment slightly improves the EQE in the broad spectral range of 400-1000 nm,
251 presumably due to the sulfurization treatment passivating the recombination center in
252 the absorber and enhancing the carrier collection efficiency[12, 31]. Notably, the EQE
253 response of the treated devices starts to decrease around 1000 nm, which is related to
254 the decrease in long-wavelength absorption due to the S content increase in the absorber
255 of the processed device[32]. The bandgap (E_g) was determined from EQE curve by
256 linear extrapolation of $(\ln(1-EQE))^2$ versus wavelength (**Figure S4**)[33]. The E_g of the
257 W/O AS and With AS device are 1.14 eV and 1.15 eV, respectively, and the E_g of the

258 treated device increases slightly due to the increase in S content[34]. The integral
259 current density calculated from the EQE spectral response is displayed in **Figure S5**.
260 The integral current density of the W/O AS and With AS devices are 34.68 and 34.95
261 mA cm⁻², respectively, which are in good agreement with the J_{SC} in the J - V curves. The
262 UPS analysis can obtain the work function and valence band of the semiconductor
263 materials, which can be combined with the bandgap values to obtain the band alignment
264 of the heterojunctions[35]. The UPS curves of CdS, W/O AS film and With AS film are
265 shown in **Figures S5** and **S6**, respectively, and the calculation process of the work
266 function is shown in the supporting information (**Note2**). The calculation results show
267 that the conduction band of CdS is higher than that of W/O AS film and With AS film
268 (the band alignment schematic is shown in Figure 3f), which proves that the p-n
269 junctions of both devices are spike structures that are favorable for carrier transport
270 (Supporting information **Note3**). The conduction band offset (CBO) of the
271 heterojunction is 0.04 eV for the W/O AS device and 0.16 eV for the With AS device.
272 The slightly increased CBO of the With AS device is more conducive to the reduction
273 of interface recombination and does not affect the electron tunneling, which improves
274 the performance of the device.

275 AFM and KPFM measurements are widely used in solar cells to analysis the spatial
276 morphology and the potential distribution around the grain boundary (GB) of the
277 samples. The 2D morphology and surface potential maps of the CZTSSe absorber are
278 shown in **Figure 4**. The surface morphology of the two samples is in good agreement
279 with the SEM images. The surface potentials of the W/O AS and With AS sample are

280 shown in Figure 4b and e. The brightness of the grain boundary of the two samples is
281 significantly higher than that of the grain interior (GI), which means that the contact
282 potential difference (CPD) of the grain boundary are higher than grain interior. Higher
283 CPDs at grain boundary lead to downward bending of the bands, which attracts
284 electrons and repels holes[12, 36]. This downward bending phenomenon can promote
285 the separation of electrons and holes, leading to a reduction in carrier recombination
286 and an enhancement of carrier separation. In addition, the average potential difference
287 of W/O AS and With As samples between the GB and GI is 26 and 73 mV, respectively
288 (Figure 4g and Figure 4h, Supporting information **Note4**). It suggests that the AS
289 sulfurization treatment increases the band bending at the grain boundary[37]. Larger
290 band bending facilitates enhanced carrier separation and collection at grain boundary,
291 suggesting that the higher carrier separation efficiency after surface sulfurization
292 treatment is one of the reasons for the increase in V_{OC} .

293 The PCE of kesterite devices is limited by the level of deep traps at the interface and in
294 the absorber bulk. Since annealing of the treated devices at 280 °C leads to ion exchange
295 between the CZTSSe and AS layer, the defect property of the absorber may change
296 accordingly. In order to gain insight into the correlation between interdiffusion and
297 deep-trap states, we performed admittance spectral measurements on W/O AS devices
298 and With AS devices. The admittance spectral results are shown in **Figure 5a, c**, the
299 capacitance of the W/O AS device varies greatly with frequency, while the capacitance
300 of the With AS content device varies less between high and low frequency. The
301 significant frequency dependence of the capacitance in the W/O AS device suggests

302 that there are greater density of traps in the absorber[32, 38]. Figure 5b and e shows the
303 Arrhenius plots of the W/O AS and With AS device, the activation energy (E_a)
304 determined from the Arrhenius plots approximates the difference between the defect
305 level and the edge of the valence band (Supporting information **Note5** and **Figure**
306 **S8**)[39, 40]. The E_a for the W/O AS and the With AS device is about 308 meV and 147
307 meV, respectively. A larger E_a value usually indicates a slower hole emission rate, so
308 defects with larger activation energy are more likely to become more efficient
309 recombination centers[32]. In the CZTSSe, the deeper energy level that are located at
310 about 300 meV above the valence band defects include the acceptor defect Cu_{Sn} and the
311 donor defect V_{Se} , while another defect level 150 meV away from the valence band can
312 be attributed to the Cu_{Zn} defect[5]. For the With AS devices, the annealing at 280 °C
313 promotes ion exchange, and the S elements in the AS layer can diffuse into the absorber
314 to a greater extent, which can passivate the V_{Se} defect on the absorber surface as well
315 as in the bulk at the same time[6, 41]. Therefore, the dominant deep-energy level defects
316 in the With AS device are converted from V_{Se} to Cu_{Zn} , which is the main reason for the
317 V_{OC} enhancement in the With AS device. In contrast to V_{Se} , which deteriorates the
318 device performance by trapping carriers as a deep energy level recombination center,
319 ionization of the acceptor defect Cu_{Zn} generates a large number of hole carriers and
320 leads to a good p-type conductivity[42].

321 Temperature-dependent $J-V$ tests ($J-V-T$) are widely used to analyze carrier transport
322 mechanism in thin-film solar cells. **Figure S9** shows the $J-V-T$ curves of W/O AS and
323 With AS devices from 120 k to 300 k under dark conditions. The diode-like behavior

324 of the W/O AS device is largely suppressed at 220 K, whereas the J - V curves of the
325 With AS device show good diode characteristics even when the temperature drops to
326 160 K, proving that the With AS device has a low transport barrier[43]. The reverse
327 saturation current (J_0) and ideal factor (A) were extracted from the J - V curves. The A
328 of the With AS device showed lower temperature dependence, indicating the
329 dominance of Shockley-Read-Hall recombination in the depletion region (**Figure 6a**).
330 The A of the W/O AS device was much larger and strongly correlated with the
331 temperature, suggesting that unfavorable tunneling-enhanced recombination was
332 dominant[44]. The dominant recombination paths can be found by plotting $\ln(J_0)$
333 against $1/kT$ and calculating the slope E_A (Interface recombination activation energy,
334 Figure 6b). E_A close to E_g indicates that bulk recombination dominates; whereas E_A less
335 than E_g implies that interface recombination is dominant[44, 45]. The E_A of the W/O
336 AS and With AS devices are 0.79 eV and 0.95 eV, respectively. The E_A values of With
337 AS devices are close to the bandgap, indicating that the AS sulfurization treatment
338 significantly passivates the interface recombination.

339 The carrier concentration of absorber and recombination property of heterojunction
340 were investigated by CV and DLCP. Figure 6c is the CV and DLCP data for the W/O
341 AS and the With AS device. The carrier density (N_{CV} and N_{DL}) and the width of
342 depletion region (W_d) derived from the DLCP data are shown in **Table 3**. The W_d is
343 similar for both samples, but that the carrier density (zero bias) is larger for the With
344 AS device. The carrier density of With AS device increases from 5.40×10^{16} to $6.66 \times$
345 10^{16} cm^{-3} , which is attributed to the transformation of the dominant defect from V_{Se} to

346 Cu_{Zn} . In general, DLCP was only includes bulk defects, the CV was also includes
347 interface defects[29, 46]. Therefore, the interface defect density (N_{IT}) can be obtained
348 by comparing $N_{\text{CV}}-N_{\text{DLCP}}$. The N_{IT} value estimated for the W/O AS and With AS device
349 were 3.34×10^{16} and $4.70 \times 10^{15} \text{ cm}^{-3}$, respectively. The interface defects were reduced
350 by an order of magnitude after the sulfurization treatment. Such a considerable decrease
351 in N_{IT} strongly confirms the superiority of the heterojunction interface of With AS
352 devices, which reduces the carrier recombination of heterojunction and accelerates the
353 carrier transport at the interface[39, 47]. The carrier transport characteristics of the
354 devices were analyzed by EIS, and the correlation curves and fitting results are
355 displayed in **Figure S10** and Table 3. The inset of Figure S10 shows the equivalent
356 circuit diagram of the CZTSSe solar cell, and the EIS curves were fitted to obtain the
357 series resistance (R_s^*), recombination resistance (R_{rec}), and chemical capacitance (C_{rec}).
358 The smaller R_s^* and larger R_{rec} of the AS devices imply that carrier recombination in
359 the devices is effectively suppressed[48, 49]. According to the diffusion-recombination
360 model, the minority carrier lifetimes (τ) of 0.59 and 2.33 microseconds for the two
361 devices, indicating that the sulfurization treatment significantly improves the carrier
362 transport dynamics of the devices.

363 To further evaluate the carrier lifetime in fully working devices, the W/O AS and With
364 AS device were tested for TPV, where photocarriers are generated under pulsed light
365 irradiation, free electrons and holes are produced and a photovoltage is generated. Once
366 the incident light is switched off, the voltage starts to decay due to transient non-
367 radiative recombination of electrons and holes at possible defect locations[2, 50].

368 Figure 6d shows the TPV results for the W/O AS and the With AS device. Based on the
369 results of the single-exponential model fitting, it is found that the TPV lifetime (τ_{TPV})
370 of the With AS device increases from 10.38 μs to 12.89 μs . The longer decay time
371 provides more opportunity for carriers to be extracted from the absorber to the
372 electrodes, which greatly reduces the carrier recombination. We know that a relatively
373 long decay time means fewer non-radiative recombination sites in the intact device.
374 Therefore, the AS sulfurization treatment reduces the defects in the CZTSSe, which
375 reduces the recombination of free carriers and facilitates carrier collection and cell
376 performance.

377 The improvement in charge transport induced by sulfurization-enhanced carrier
378 collection and separation at grain boundary may be the direct cause of the enhanced
379 electrical property of the devices. EBIC can help us to further investigate the transport
380 of electrons across grain boundary at microscopic level. The SEM cross-section, EBIC
381 mapping is shown in Figure 6e, f, Figure 6g shows the normalized EBIC signals of the
382 W/O AS and With AS device along the grey dashed line. Bright regions in the EBIC
383 image imply high carrier collection efficiency, and the depths represent minority carrier
384 diffusion lengths[51, 52]. Near the CdS/CZTSSe interface, both samples show strong
385 carrier collection, and the reason for the strong EBIC signal near the interface is the
386 strong electric field in the region. It indicates high carrier collection efficiency near the
387 heterojunction. The EBIC signal is significantly weaker away from the p-n junction,
388 which was limited by the possible presence of significant recombination and/or carrier
389 transport barriers. Compared to W/O AS device. With AS device have stronger EBIC

390 signal at the heterojunction interface (**Figure S11**, non-normalized EBIC line scan),
391 implying that With AS device have stronger built-in electric field, as reflected in the
392 KPFM data[53, 54]. Meanwhile, the EBIC signal of the With AS device decreases
393 slower and has higher intensity near the back interface (Figure 6g, normalized EBIC
394 line scan), indicating that the AS sulfurization treatment effectively improves the carrier
395 collection capability, the carrier diffusion length is extended and the charge collection
396 process is improved.

397 **Conclusion**

398 This manuscript proposes a simple and effective method to simultaneously treat surface
399 and bulk of CZTSSe device by a pre-soaking and spin-coating-annealing sulfurization
400 for the first time. The champion CZTSSe device based on the optimal AS solution
401 sulfurization treatment duration obtain PCE of 13.19%. This strategy adds an annealing
402 step to the surface sulfurization process, which promotes elemental diffusion and
403 passivates surface and bulk defects of CZTSSe devices. The removal of secondary
404 phase from the absorber surface facilitates better p-n junction quality and reduces
405 interface carrier recombination. Further study shows that the band bending at grain
406 boundary of the treated samples is larger, which is more favorable for the carrier
407 separation and collection ability. The conversion of the dominant deep energy level
408 defect from V_{Se} to Cu_{Zn} reduces the recombination of free carriers. Stronger EBIC
409 signals and slower decay rates indicate that the AS sulfurization treatment effectively
410 improves the carrier collection, extends the carrier diffusion length and improves the
411 charge collection process. The present work provides a new idea and easy-to-handle

412 method for removing the bulk defects and the front interface of the secondary phase-
413 time-modified high-efficiency kesterite solar cells on the absorber layer surface.

414

415 **Declaration of Competing Interest**

416 The authors declare no conflict of interest.

417

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423

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643

644 **Table 1** Photovoltaic parameters of reference, A and B solar cells.

	REF	A1	A2	B1	B2	B3
J_{sc} (mA/cm ²)	37.27	37.82	37.54	37.34	37.47	37.35
V_{oc} (V)	0.494	0.493	0.495	0.510	0.531	0.514
FF (%)	63.10	63.29	63.74	64.37	66.30	65.55
PCE (%)	11.26	11.80	11.84	11.98	13.19	12.32

645

646 **Table 2** Diode parameters, bandgap, defect recombination activation energy and deep

647 defect density for W/O AS and With AS devices

	R_s (Ω)	R_{sh} (Ω)	A	J_0 (mA cm ⁻²)	E_g (eV)	E_a (meV)	N_T (cm ⁻³)
W/O AS	1.41	383	1.64	2.70×10^{-5}	1.14	308	3.10×10^{16}
With AS	0.71	441	1.50	1.57×10^{-5}	1.15	147	1.10×10^{16}

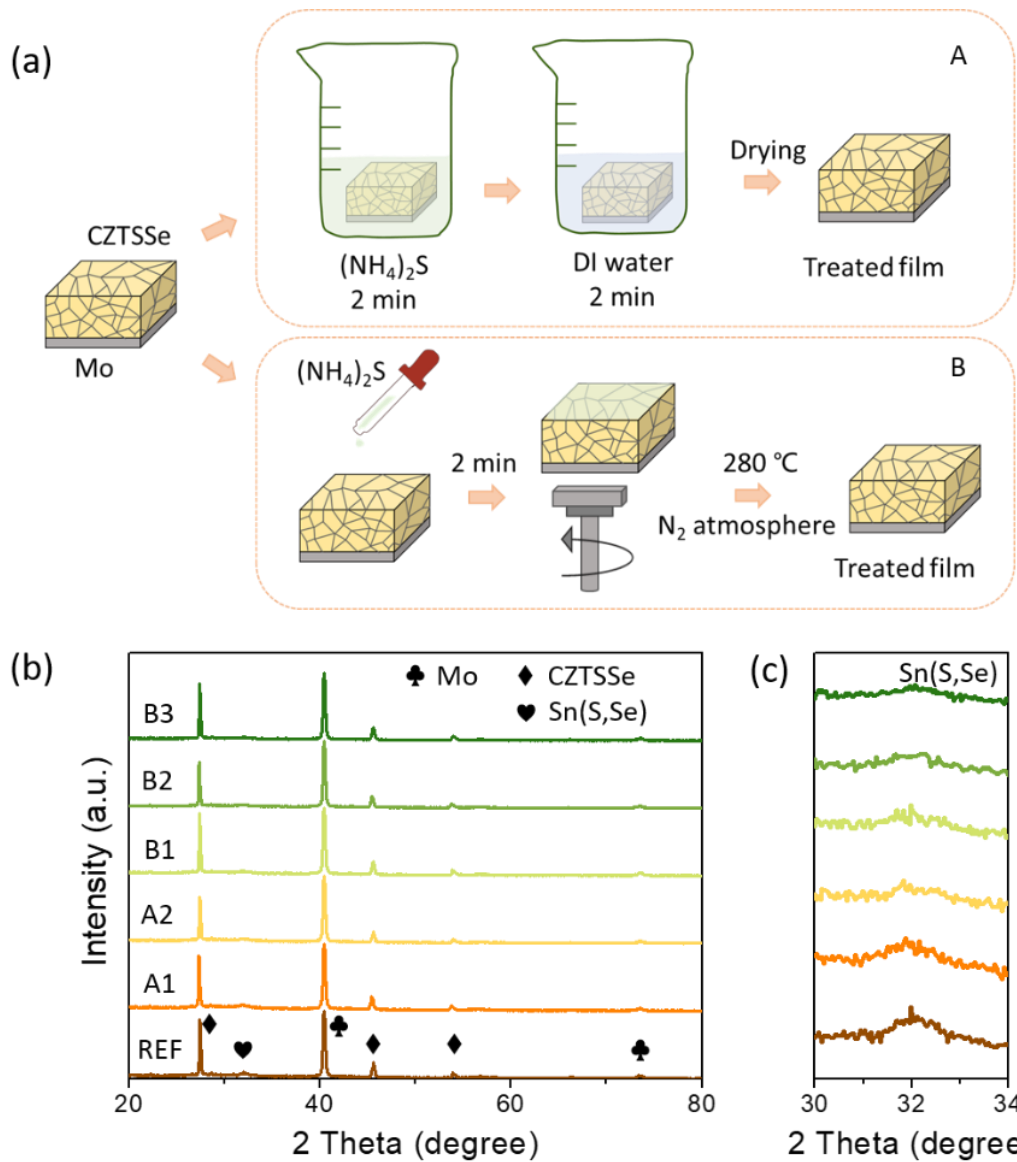
648

649 **Table 3** Calculated results of CV, DLCP, EIS and TPV analysis.

	N_{CV} (cm ⁻³)	N_{DL} (cm ⁻³)	W_d (μ m)	N_{IT} (cm ⁻³)	R_{rec} (Ω)	R_s^* (Ω)	C_{rec} (nF)	τ (μ s)	τ_{TPV} (μ s)
W/O AS	8.74×10^{16}	5.40×10^{16}	0.191	3.34×10^{16}	30.36	25.14	19.43	0.59	10.38
With AS	7.13×10^{16}	6.66×10^{16}	0.190	4.70×10^{15}	46.85	71.33	49.73	2.33	12.89

650

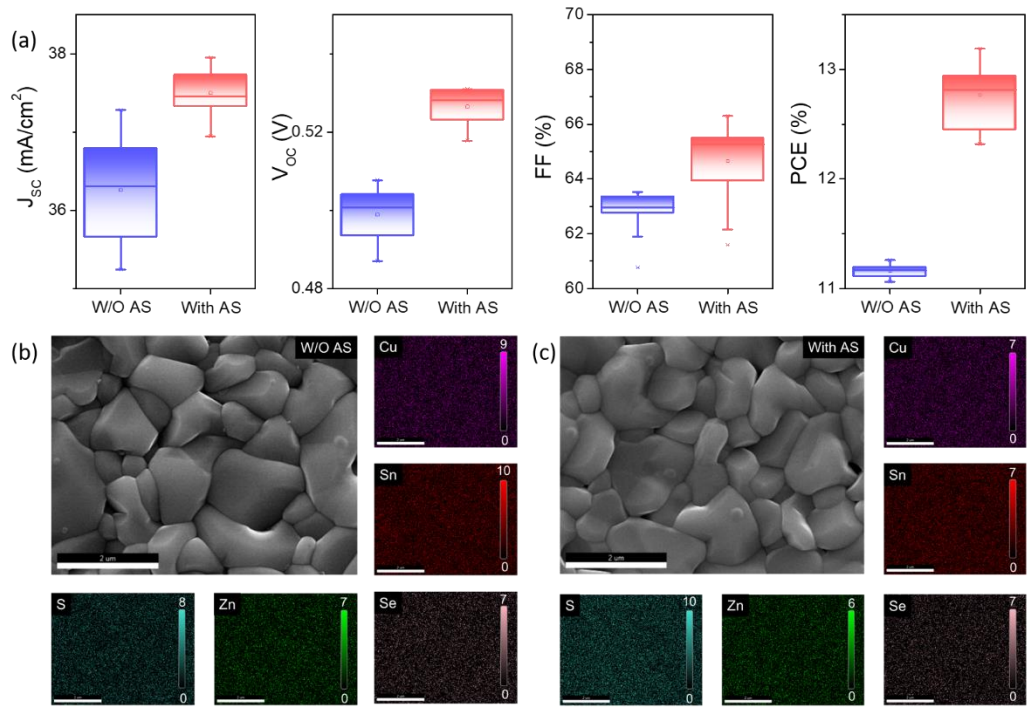
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653

654 **Figure 1** (a) Illustration of different AS sulfurization treatment processes, (b) XRD
 655 patterns of the reference sample, sample A and sample B, (c) The enlarged characteristic
 656 of (112) peak.

657



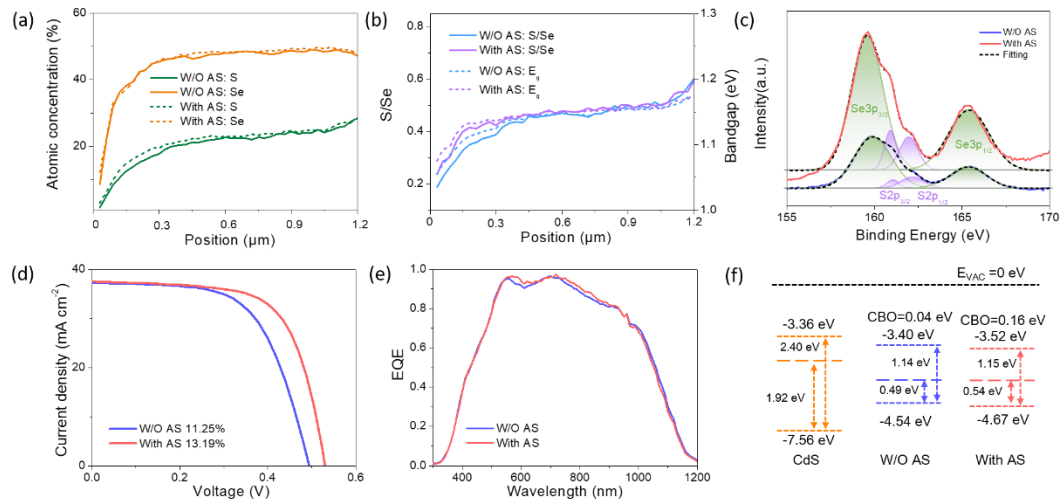
658

659 **Figure 2** (a) Statistical boxplot of J_{sc} , V_{oc} , FF and PCE for W/O AS and With AS

660 device, (b) SEM image and EDS mapping of the W/O AS film, (c) SEM image and

661 EDS mapping of the With AS film.

662



663

664 **Figure 3** (a) S and Se elemental line scans of W/O AS and With AS films, (b) S/Se

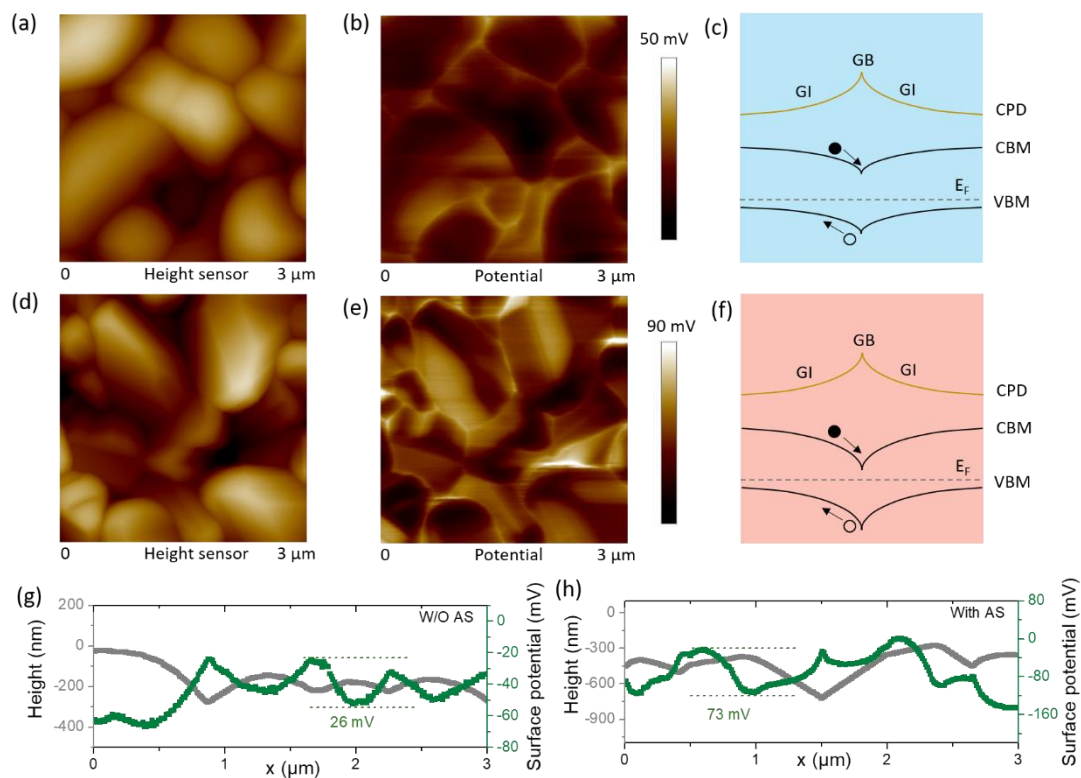
665 profiles and bandgap profiles of W/O AS and With AS films, (c) XPS analysis of S 3p

666 for the W/O AS and With AS film, (d) *J-V* characteristics of CZTSSe device W/O AS

667 and With AS, (e) EQE of W/O AS and With AS device, (f) heterojunction band

668 alignment schematic for W/O AS and With AS devices.

669



670

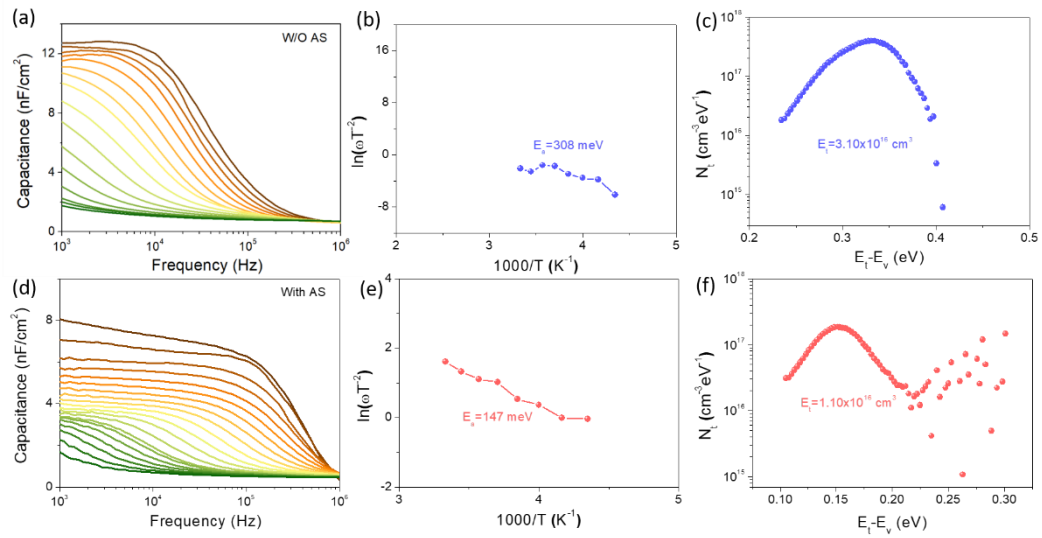
671 **Figure 4** AFM and KPFM of the (a, b) W/O AS film and (d, e) With AS film. Schematic

672 of the band diagram and CPD near grain boundary of (c) W/O AS film and (f) With AS

673 film. The potential variation of (g) W/O AS film and (h) With AS film.

674

675



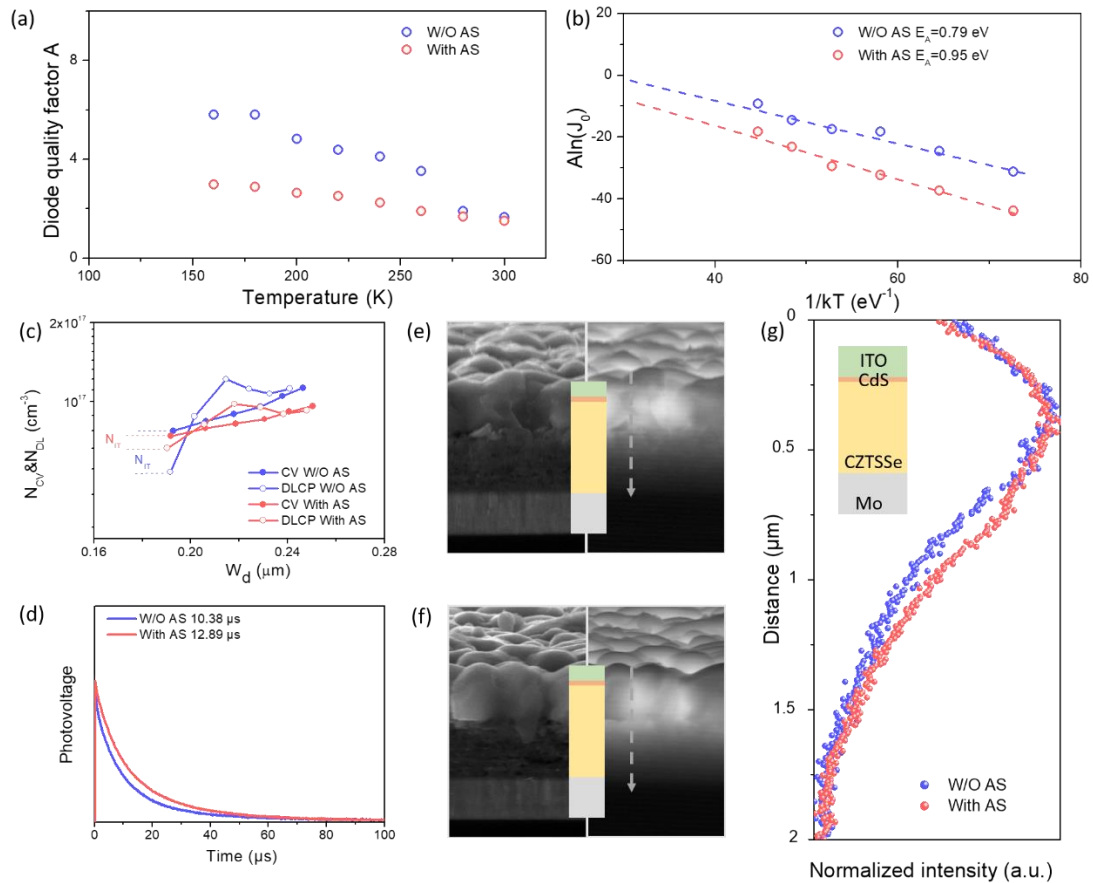
676

677 **Figure 5** Admittance spectral results for (a) W/O AS, (d) With AS, from the inflection

678 points of the C - f - T results, the Arrhenius plots of (b) W/O AS, (e) With AS, the defect

679 density of states for (c) W/O AS, (f) With AS.

680



681

682 **Figure 6** (a) Temperature dependence of ideal factor of W/O AS and With AS device,

683 (b) $\ln(J_0)$ versus $1/kT$ plot of W/O AS and With AS device, (c) The plot of CV and

684 DLCP for devices W/O AS and With AS, (d) TPV spectra of W/O AS and With AS

685 device, cross-sectional SEM and EBIC images for (e) W/O AS device and (f) With AS

686 device, (g) the intensity profiling of the dashed line in EBIC images.

687

688 **Supporting information**

689 **Suppressing Surface and Bulk Effect enables High Efficiency**

690 **Solution-Processed Kesterite Solar Cells**

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702

703 **Supplementary Notes**

704 **Supplementary Note1** Bandgap calculation based on S/Se

705 The bandgap values of $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$ for different Se contents can be calculated

706 using the sophisticated hybrid functional HSE (Heyd-Scuseria-Ernzerhof) reported by

707 Chen et al. with the following formula:

708 $E_g(x) = (1-x)E_g(\text{CZTS}) + xE_g(\text{CZTSe}) - bx(1-x)$ (S1)

709 where Se content is x , S content is $1-x$, $E_g(\text{CZTS})$ is 1.5 eV, $E_g(\text{CZTSe})$ is 0.96 eV, and
710 b denotes bandgap bending with a value of 0.07 eV[1].

711

712 **Supplementary Note2** UPS analysis

713 The work function (ϕ) is obtained from the following equation:

$$714 \quad \phi = h\nu - E_{\text{cut off}} \quad (\text{S2})$$

715 where $h\nu$ is 21.22 eV (He I source) and $E_{\text{cut off}}$ is based on the extrapolation of the linear
716 region of high binding energy[2].

717

718 **Supplementary Note3** Calculation of CBO

719 The band alignment at the heterojunction contains both spike-type and cliff-type. When
720 the electron affinity energy of the buffer layer is larger than that of the absorber, the
721 CBO at the heterojunction is negative, and the band alignment at this time is cliff-type.

722 The cliff-type band alignment will strongly increase the interface recombination and
723 decrease the V_{OC} . And when the electron affinity energy of the buffer layer is smaller
724 than that of the absorber, the CBO at the heterojunction is positive, and the band
725 alignment is spike-type in this case. Spike-type band alignment is favorable to prevent
726 electron return and reduce interface recombination, but excessive spike (too large CBO)
727 affects the electron tunneling effect at the interface thus deteriorating the device
728 performance. Relevant literatures show that CBO is optimal between 0-0.4 eV, in which
729 the larger CBO is more favorable to reduce interface recombination. In this work, the
730 CBO at the heterojunction of the With AS device is slightly increased due to the

731 sulfurization treatment that improves the S/Se content in the near-surface region of the
732 absorber layer, favoring the reduction of heterojunction interface recombination[3].

733

734 **Supplementary Note4** KPFM analysis

735 KPFM is used to determine the electrostatic potential change between the probe and
736 the sample due to the localized surface potential change. The brightness of the grain
737 boundary (GB) of both samples is significantly higher than that of the grain interior
738 (GI), and the potential difference between GI and GB can be expressed by the following
739 equation:

$$740 \quad \Delta \text{CPD} = \varphi_{\text{GI}} - \varphi_{\text{GB}} = eV_{\text{CPD(GB)}} - eV_{\text{CPD(GI)}} \quad (\text{S3})$$

741 where φ_{GI} and φ_{GB} are the potentials at the GI and GB, respectively[4].

742

743 **Supplementary Note5** Admittance spectra analysis

744 Admittance spectral measurements are used to estimate the defect level within the
745 bandgap. The inflection frequency ω_0 of each admittance spectral curve is determined
746 by the corner frequency point at the maximum of the $-\omega dC/d\omega$ plot (Figure S9). The
747 fitting equation for the Arrhenius plot is[5]:

$$748 \quad \omega_0 = 2\pi\nu_0 T^2 e^{-\frac{E_a}{kT}} \quad (\text{S4})$$

749 where ω_0 is the inflection frequency, E_a is the depth of the defect relative to the edge of
750 the valence band, and ν_0 is the exponential prefactor. In this case, the activation
751 energy E_a determined from the Arrhenius diagram is approximated as the energy

752 difference between the defect energy level and the valence band edge. The defect
753 density obtained from the *C-f* scan is calculated as follows:

$$754 \quad E_a = kT \ln\left(\frac{2\pi v_0 T^2}{\omega}\right) \quad (\text{S5})$$

$$755 \quad N_T = -\frac{V_{bi}}{W_d} \cdot \frac{dC}{d\omega} \cdot \frac{\omega}{kT} \quad (\text{S6})$$

756 where N_T is the defect density, W_d is depletion width and V_{bi} is the built-in voltage[6].

757

758 **Supplementary Note6** EIS analysis

759 EIS can be used to determine minority carrier (electron) recombination to characterize
760 carrier transport behavior. The EIS data were fitted using an equivalent circuit model,
761 which consists of a chemical capacitor (C_{rec}) connected by a shunt composite resistor
762 (R_{rec}) and a series resistor (R_s^*), and the measured carrier lifetimes corresponded to the
763 carrier transport behavior within the absorber layer close to the CdS/CZTSSe interface.
764 According to the diffusion-recombination model, the minority carrier lifetime can be
765 calculated according to the following equation[7]:

$$766 \quad \tau = R_{rec} \times C_{rec} \quad (\text{S7})$$

767

768 **Supplementary Note7** CV and DLCP analysis

769 CV and DLCP are often used to analyze carrier concentration and depletion width in
770 thin film solar cells. The formulas for the calculations are as follows[8]:

$$771 \quad N_{CV} = \frac{C^3}{qA^2 \epsilon_0 \epsilon} \left(\frac{dC}{dV}\right)^{-1} \quad (\text{S8})$$

$$772 \quad W_{d-CV} = \frac{\epsilon_0 \epsilon A}{C} \quad (\text{S9})$$

773
$$N_{DL} = -\frac{C_0^3}{2q\varepsilon_0\varepsilon A^2 C_1} \quad (S10)$$

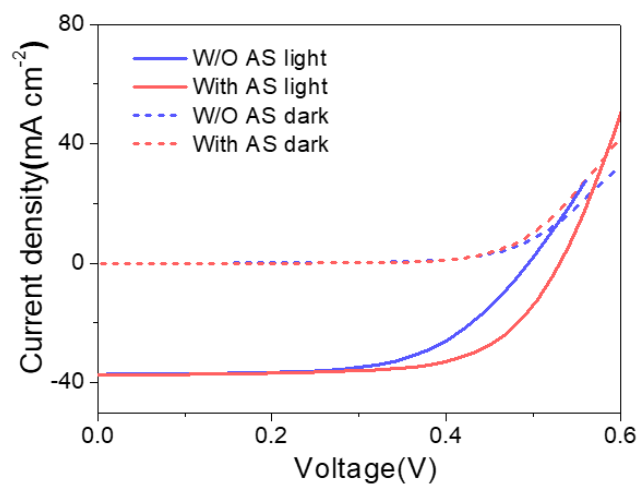
774
$$W_{d-DL} = \frac{\varepsilon_0\varepsilon A}{C_0} \quad (S11)$$

775 Where ε and ε_0 stand for the dielectric constant of the CZTSSe and vacuum dielectric
776 constant, respectively; C , A and q is the measured capacitance, the active area of the
777 cell, and elementary charge, C_0 and C_1 are two quadratic fitting parameters derived
778 from the DLCP. Besides, The CV measurement is more sensitive to the interface state
779 (N_{IT}) than the DLCP, so the interface state density can be obtained from the difference
780 between the CV and the DLCP:

781
$$N_{IT} = N_{CV} - N_{DL} \quad (S12)$$

782

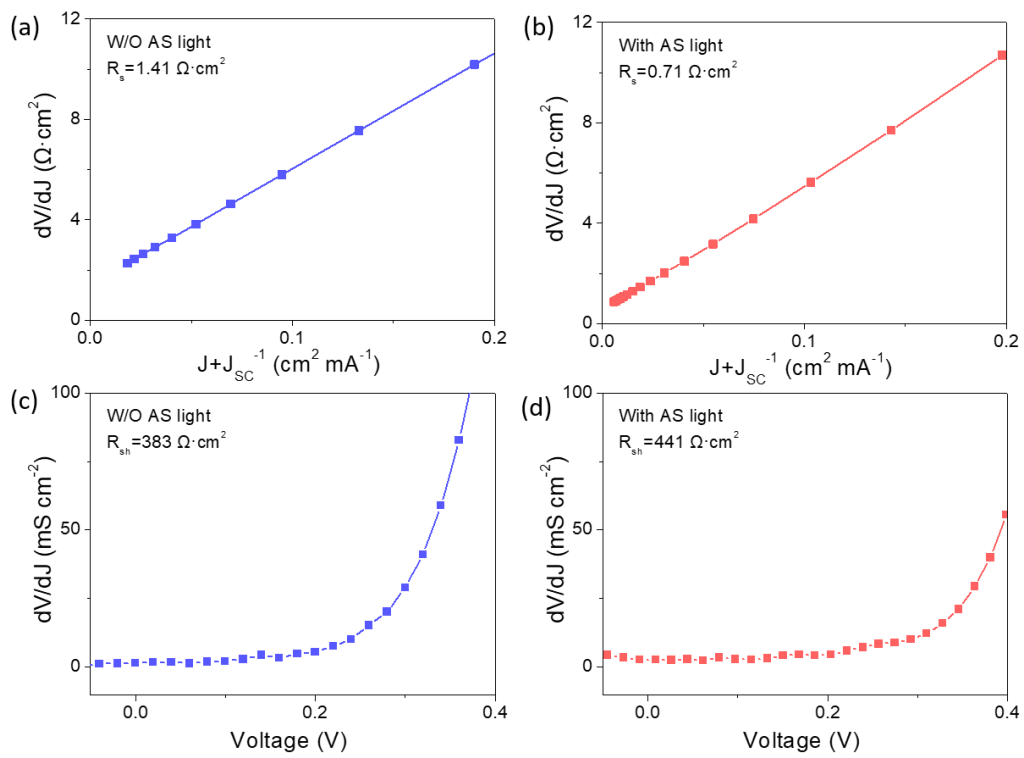
783 **Supplementary Figures**



784

785 **Figure S1** Light-state and dark-state *J-V* curves for W/O AS and With AS devices.

786

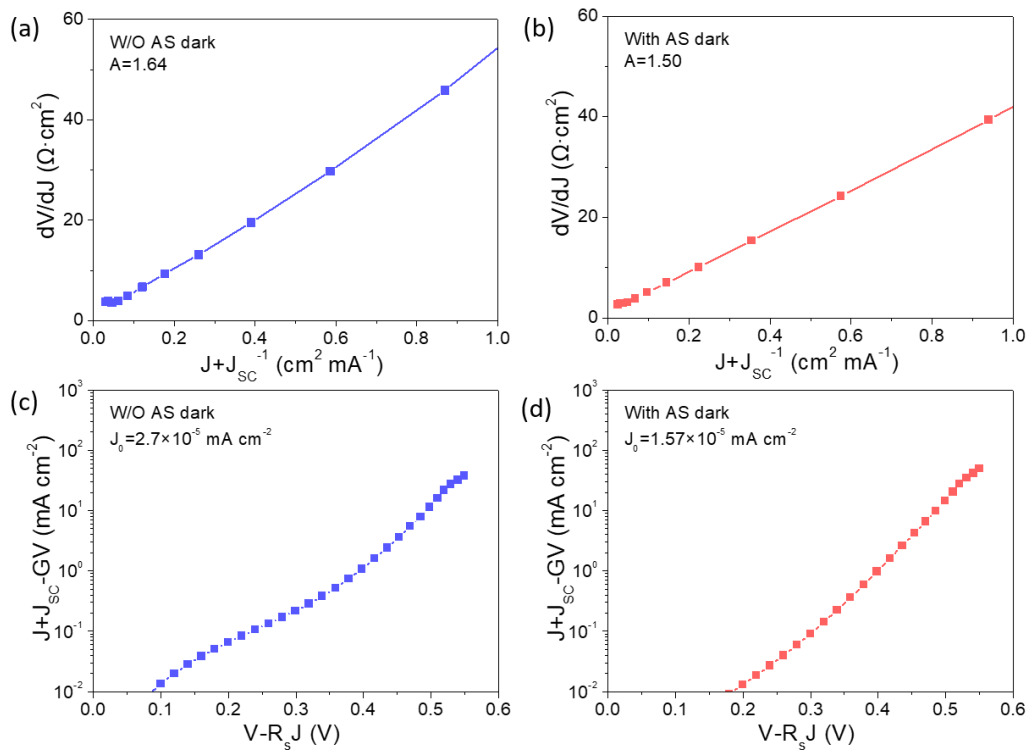


787

788 **Figure S2** Series resistance (a, b) and parallel resistance (c, d) for W/O AS and With
 789 AS devices. (a) and (c) correspond to W/O AS device, (b) and (d) correspond to With
 790 AS device.

791

792



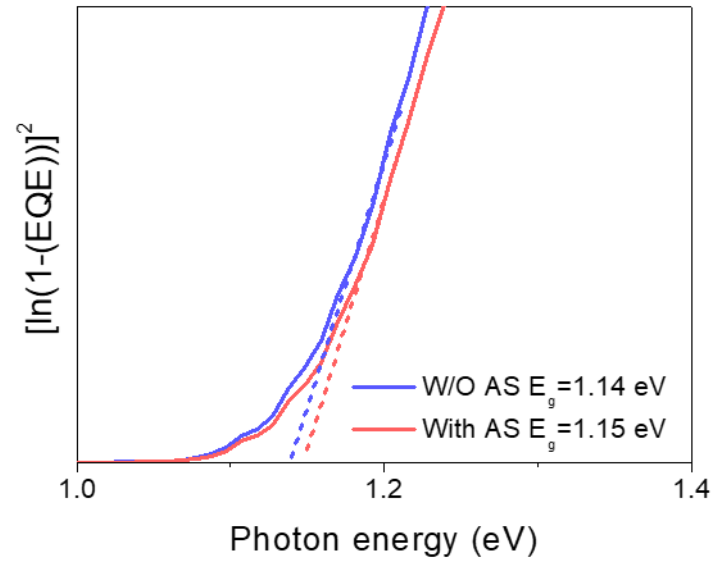
793

794 **Figure S3** Diode ideal factor (a, b) and reverse saturation current (c, d) for W/O AS

795 and With AS devices. (a) and (c) correspond to W/O AS devices, (b) and (d)

796 correspond to With AS devices.

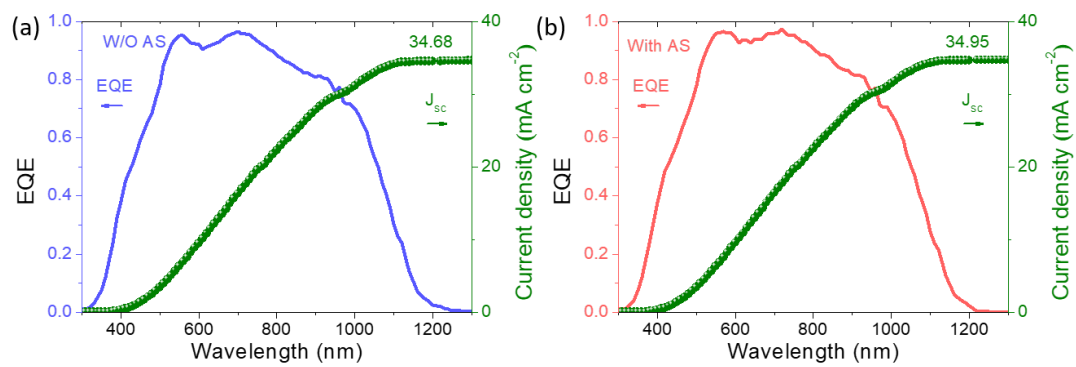
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799 **Figure S4** Bandgap of W/O AS and With AS devices calculated from EQE curves.

800

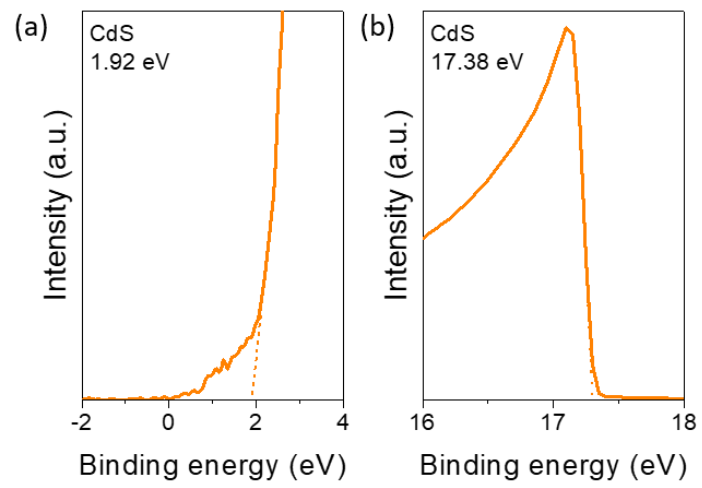


801

802 **Figure S5** Integral current density of W/O AS (a) and With AS (b) devices calculated

803 from EQE curve.

804

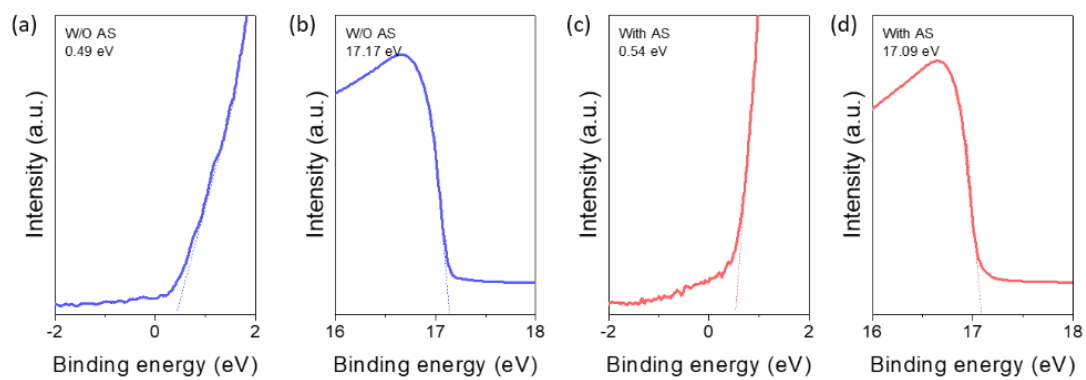


805

806 **Figure S6** UPS curve for CdS. (a) correspond to low binding energy, (b) correspond

807 to high binding energy.

808

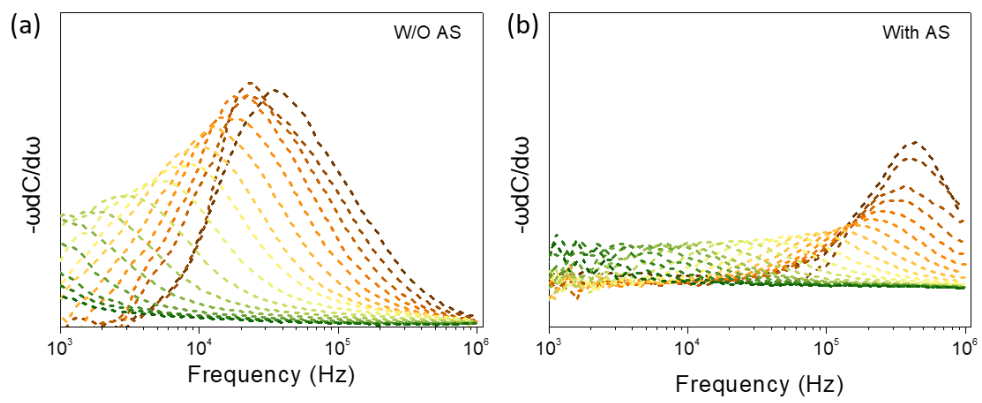


809

810 **Figure S7** UPS curves for W/O AS (a, b) and With AS films (c, d). (a) and (c)

811 correspond to low binding energy, (c) and (d) correspond to high binding energy.

812

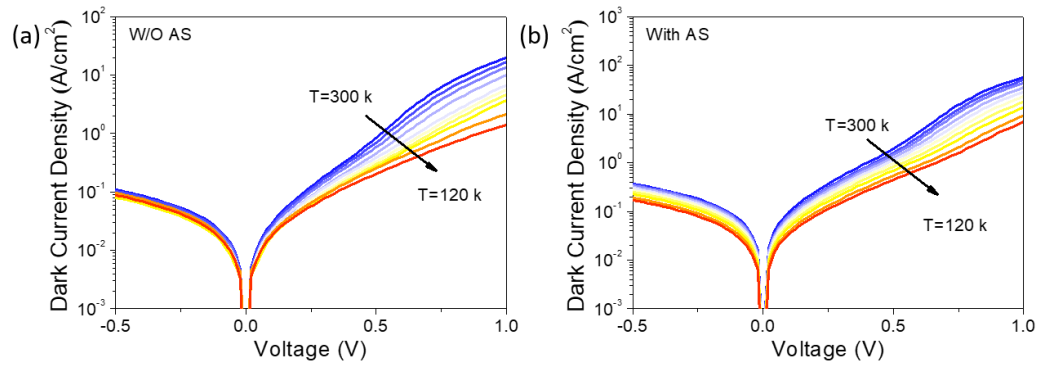


813

814 **Figure S8** Plots of $-\omega dC/d\omega$ vs. frequency at different temperature for W/O AS (a)

815 and With AS devices (b).

816

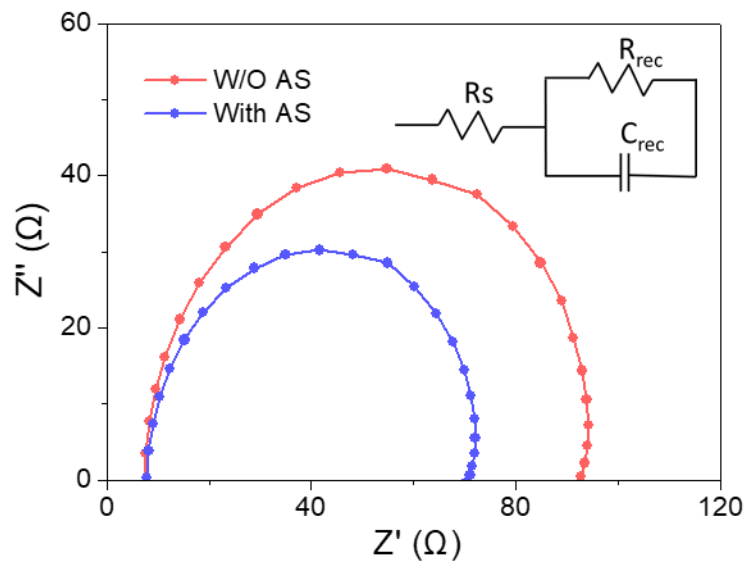


817

818 **Figure S9** Temperature-dependent dark J - V curves of W/O AS device (a) and With AS

819 device (b)

820

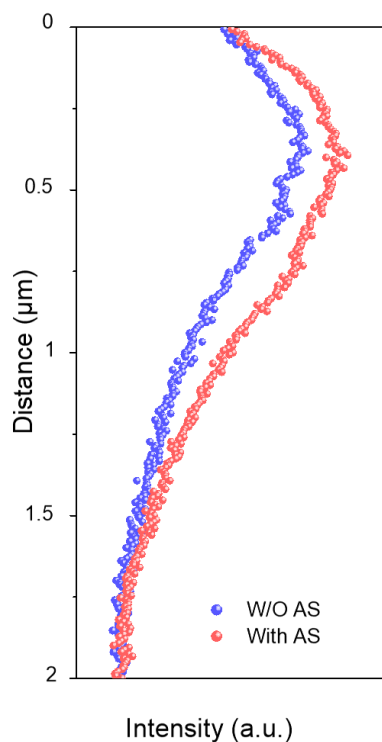


821

822 **Figure S10** The EIS curves for the W/O AS and With AS devices, inset shows the

823 equivalent circuit diagram.

824



825

826 **Figure S11** W/O AS and With AS device non-normalized EBIC signal line scanning.

827

828

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