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1                   **Comparative study of  $\text{Cu}_2\text{ZnSnSe}_4$  solar cells growth on**  
2                   **transparent conductive oxides and molybdenum substrates**

3

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5

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9

10 Abstract

11  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) thin films have been synthesized by cosputtering followed by a  
12 selenization treatment on Mo and transparent conductive oxide (TCO) coated soda lime glass  
13 substrates, such as ZnO:Al and SnO<sub>2</sub>:F (FTO). The aims of the present work is to investigate  
14 the impact of the TCO substrates on the CZTSe growth, the reactions at the back contact and  
15 the electrical properties of solar cells. The results show that the morphology of CZTSe is  
16 affected by the TCO back contacts. It is found that TCO acts as a diffusion barrier of Na from  
17 soda lime glass to CZTSe. Thus low incorporation of Na during the annealing could explain  
18 the difference in grain size of CZTSe deposited on TCO. Moreover it is evidenced chemical  
19 reactions between TCO and CZTSe which affects the interface. While the efficiency up to 8  
20 % is obtained for CZTSe based solar cells deposited on Mo substrate, the efficiency drops to  
21 2.3 % for the solar cells deposited on FTO. The low efficiency is explained by the  
22 recombination at the back contact due to the formation of a very thin layer of ZnO at the  
23 CZTSe/FTO interface.

## 24 I. Introduction

25

26 The polycrystalline kesterite  $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$  (CZTSSe) solar cell is a promising thin-film  
27 solar cell technology owing to the abundance of its constitutive elements and its low  
28 production cost. Solar cells with a conversion efficiency up to 12.7% has been reported [1].  
29 Most of the CZTSSe based solar cells have been fabricated on Mo substrate which has many  
30 advantages (good thermal stability, ohmic contact with CZTSSe) [2,3]. However its opaque  
31 nature limits its use as a back contact for semi-transparent, bifacial or tandem solar cells. Thus  
32 the use of transparent conductive oxides (TCO) as back contact can offer new possibilities for  
33 the application of CZTSSe absorber. The most common TCOs used in chalcogenide solar  
34 cells are tin doped indium oxide ( $\text{In}_2\text{O}_3:\text{Sn}$  or ITO), fluorine doped tin oxide ( $\text{SnO}_2:\text{F}$  or FTO)  
35 or aluminium doped zinc oxide ( $\text{ZnO}:\text{Al}$ ).

36 Many groups have investigated the  $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$  (CIGS) based solar cells deposited on TCO  
37 [4-9]. The best efficiencies up to 15.2% are obtained using  $\text{In}_2\text{O}_3:\text{Sn}$  (ITO) as back contact  
38 [4]. In the case of kesterite based solar cells only very few studies have been reported using  
39 this type of back contact. CZTSSe solar cells have been deposited on ITO [10-14] and best  
40 efficiencies up to 5.8 % are reached under bifacial illumination [15]. The low efficiency in  
41 these solar cells is reported to be due to an interfacial reaction at ITO back contact, which  
42 induces the Indium diffusion into the CZTSSe absorber and formation of an oxide  $\text{SnO}_x$  thin  
43 layer, thus degrading the CZTSSe rear interface [12]. CZTSSe based solar cells have also  
44 been deposited on FTO [13,16-18], reaching efficiencies up to 7.7% using a Mo nanolayer at  
45 the CZTSSe/FTO interface [19]. Lee & al. reported a superstrate CZTSSe based solar cells  
46 deposited on ZnO wire and completed with a graphite electrode reaching efficiencies of 1.2 %  
47 [20].

48 In this work, we compared the growth of  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) deposited on two different  
49 glass coated TCOs : AZO ( $\text{ZnO}:\text{Al}$ ) and FTO. The results are compared to cells with classical  
50 Mo back contact [21,22]. The effect of substrate combined with the deposition temperature of  
51 the absorber on morphology, composition, crystallinity of CZTSe and the optoelectronic  
52 properties of the solar cells will be discussed.

53

## 54 II. Experimental section

55

56 Thin Cu-Zn-Sn precursors were deposited on Mo, SnO<sub>2</sub>:F (3% of F) (FTO) and ZnO:Al (3%  
57 of Al) (AZO) coated soda lime glass substrates using RF magnetron co-sputtering from Cu,  
58 Zn and Sn targets at room temperature with [Cu] / ([Sn]+[Zn]) and [Zn] / [Sn] values  
59 respectively close to 0.7 and 1.2 (Cu-poor, Zn-rich). These films were then annealed inside a  
60 graphite box under a pure selenium atmosphere (Se) provided by an amount of 60 mg of Se  
61 pellets. The annealing was done at 600 °C for 15 min [21]. For optoelectronic characterization  
62 of the cells, after annealing, a layer of 50 nm of CdS was deposited on the CZTSe absorber by  
63 chemical bath deposition and a double layer of ZnO:i / AZO of around 350 nm was deposited  
64 by sputtering to complete the solar cell. Before the deposition of the CdS layer, surface  
65 etching has been underwent on the CZTSe absorber with KCN, KMnO<sub>4</sub>+H<sub>2</sub>SO<sub>4</sub>+Na<sub>2</sub>S and  
66 (NH<sub>4</sub>)<sub>2</sub>S [23].

67 The AZO as back contact was grown on a 3-mm-thick soda-lime glass following the same  
68 procedure than the AZO used for the front contact. The layer was deposited by radio-  
69 frequency (RF) sputtering using an AZO ceramic target under argon plasma and O<sub>2</sub> flux and  
70 at a RF power density of 3W/cm<sup>2</sup>. Two thicknesses of AZO (500 nm and 1300 nm) were  
71 compared.

72 The FTO substrate is a commercially available product from Solems. The FTO layer was  
73 deposited by spay pyrolysis on a 2-mm-thick soda-lime glass. Its thickness is 600-700 nm  
74 with a roughness of ±40 nm. The sheet resistance of the samples was measured by 4-point  
75 probe.

76 As the CZTSe is annealed at high temperature (500 to 550°C) under Se atmosphere and in  
77 order to evaluated the evolution of the TCO parameters under similar conditions, the AZO  
78 and FTO layers were also annealed separately. The substrates were placed with 50 mg of Se  
79 pellets in the graphite box inserted in a tubular furnace under atmospheric pressure of Ar. A  
80 lower amount of Se has been used as ZnO layer is directly in contact with the Se atmosphere.  
81 The box was heated at 500°C or 600°C with a linear heating ramp of 15 min, and the  
82 temperature was maintained for 45 min.

83 The composition of the absorber has been studied by Glow discharge optical spectroscopy  
84 (GD-OES) measurements. The calibrated signals with a reference give quantitative  
85 information of the presence of the elements in the samples. The crystallinity of the absorbers  
86 was examined by X-ray diffraction (XRD) with a Panalytical Empyrean X-ray diffractometer  
87 using CuK<sub>α</sub> radiation (1.5419Å) in the classical Bragg-Brentano and grazing incidence X-ray

88 diffraction (GIXRD) setups. An incidence angle of  $0.5^\circ$  has been used in order to probes the  
89 whole thickness of layers with XRD and to obtain an optimal signal. Raman microprobe  
90 measurements were conducted using a HR800-UV Horiba Jobin Yvon spectrometer with 532  
91 nm- and 385 nm lasers and a X50 objective.

92 In order to characterize the interface between the TCO and the CZTSe absorber, the sample  
93 was encapsulated using a transparent epoxy and a 3-mm borosilicate glass and then a lift-off  
94 was performed allowing the mechanical separation of the CZTSe layer from the glass/back  
95 contact [2,3].

96 The surface morphology of the samples were investigated by a scanning electron microscopy  
97 (SEM) using a Leo Supra 35 field emission gun (FEG) with 15 kV voltage. The electrical  
98 properties of the solar cells were characterized by current voltage measurements in dark and  
99 light illumination at  $25^\circ\text{C}$  (AM1.5 global spectrum). Quantum efficiencies were collected  
100 using Oriel IQE-200 <sup>TM</sup> instruments.

101

### 102 III. Results and discussions

103 The chemical, electrical and optical properties of ZnO:Al (AZO) and SnO<sub>2</sub>:F (FTO) layers  
104 can change during the CZTSe process at high temperature ( $600^\circ\text{C}$ ) under Se atmosphere. In  
105 order to evaluated the evolution of the TCO parameters under similar conditions, The  
106 Glass/600-nm-thick AZO, Glass/1300-nm-thick AZO and the Glass/650-nm-thick FTO  
107 substrates were placed with 50 mg of Se pellets in graphite box under atmospheric pressure of  
108 Ar. The evolution of the square resistance of samples before and after annealing at  $500^\circ\text{C}$  and  
109  $600^\circ\text{C}$  are presented on Fig.1. The FTO layer seems to be perfectly stable at high temperature  
110 as the square resistance remains constant at about  $6\ \Omega/\square$  whatever the annealing temperature.  
111 For the annealing of the 500-nm-thick AZO, both  $500^\circ\text{C}$  and  $600^\circ\text{C}$  under Se atmosphere lead to  
112 a dramatically increase of the sheet resistance while annealing of the 1300-nm-thick AZO  
113 only moderately increases. Indeed, under the same annealing conditions at  $600^\circ\text{C}$ , the sheet  
114 resistance is considerably lower for a 1300 nm-thick AZO layer ( $16\ \Omega/\square$ ) than the 500 nm-  
115 thick AZO layer ( $200\ \Omega/\square$ ). This means that the AZO degradation seems to be a surface effect  
116 explaining the lower sheet resistance of the 1300-nm-thick AZO layer.

117 In order to confirm this hypothesis the crystallinity and the morphology of glass/1300-nm-  
118 thick and the Glass/650-nm-thick FTO were analyzed by XRD and SEM measurements

119 before and after annealing. SEM cross sectional images of FTO and AZO (1300nm)  
120 substrates before and after Se annealing are shown in Fig.2. While no change is observed for  
121 FTO based samples before and after annealing (Fig.2a and 2b), Fig.2c and 2d reveal  
122 morphological changes of AZO induced by the Se annealing. The columnar structure of the  
123 AZO layer disappears after annealing under Se and a bilayer of 1000 nm and 500 nm is  
124 observed. Moreover, the formation of holes is observed at the interface of the two layers.  
125 Differences in lattice parameter between the hexagonal crystal structure of ZnO and the cubic  
126 structure of ZnSe, may cause the formation of cavities at the interface between the ZnSe and  
127 ZnO layers.

128 Grazing incidence X-ray diffraction (GIXRD) measurements were performed on FTO and  
129 AZO coated substrates before and after annealing at 600°C under Se atmosphere. Fig.3  
130 confirms that FTO is quite stable under Se atmosphere, as the XRD diagrams are exactly the  
131 same before and after annealing.

132 It is also observed that the (103)/(002) ratio of ZnO increases from 1.3 before annealing to 2.6  
133 after annealing. In parallel the (103)/(102) ratio of ZnO increases from 6.7 before annealing to  
134 7.6 after annealing. Based on these results it appears that there is change on the preferential  
135 orientation of ZnO after annealing.

136 Moreover several new peaks in addition to ZnO peaks are observed after annealing which are  
137 assigned to ZnSe phase (PDF # 00-037-1463) confirming the formation of a thin ZnSe layer at  
138 the surface of the film as observed on SEM pictures (Fig.2d). The formation of ZnSe could  
139 result from substitution of oxygen with selenium. Reaction of oxides phases with  
140 chalcogenide phases through substitution of oxygen by the chalcogen (S, Se) have already  
141 been studied in previous works [24,25].

142 During the annealing, the transparent conducting back contact is not only in contact with Se  
143 but also with the CZTSe phase and in consequently with its associated binaries. The reactivity  
144 of the binaries with the TCO back contact can be estimated by the calculation of the standard  
145 Gibbs free energy of the reaction ( $\Delta G_f$ ). Table 1 summarizes the  $\Delta G_f$  of different reactions  
146 potentially occurring at the interface between the TCO and the CZTSe absorber [26]. If  $\Delta G_f <$   
147 0, the reaction is thermodynamically favored. The CZTSe decomposition is not possible if any  
148 reaction with the constituent binaries ( $\text{Cu}_2\text{Se}$ ,  $\text{Sn}_2\text{Se}_3$ ,  $\text{ZnSe}$ ) is thermodynamically not  
149 allowed.

150 For the AZO back-contact, the calculated  $\Delta G_f$  for the reaction between ZnO and Se is  
151 negative. Therefore, ZnSe layer can be formed at the interface between the CZTSe and the  
152 AZO. The reaction of ZnO with the Se vapors leads to the emission of  $\text{SeO}_2$  gas.

153 On the opposite, for the FTO back-contact, the calculated  $\Delta G_f$  calculated for the reactions  
154 between  $\text{SnO}_2$  and Se, and  $\text{Cu}_2\text{Se}$  are positive. Thus FTO would not react during the CZTSe  
155 formation. The CZTSe process is likely to impact the AZO layer performance leading not  
156 only to a reduction of the doping concentration but also to some thermodynamically favored  
157 reactions between CZTSe and AZO. On the opposite, the FTO layer is perfectly stable up to  
158  $600^\circ\text{C}$ . However, it is important to note that the kinetic of the reaction may be too long and  
159 that the annealing process is not at thermodynamically equilibrium. Therefore, the  
160 experimental results can differ from the conclusions based on these calculations.

161 SEM analysis of CZTSe absorber deposited on Mo, AZO, and FTO are shown in Fig.4. The  
162 films are dense whatever the substrate. However, the morphology of grains depends to the  
163 back contact. Indeed, while larger grains of CZTSe  $> 2\mu\text{m}$  are formed on Mo substrate  
164 (Fig.4a), smallest grains ( $< 1\mu\text{m}$ ) are formed on FTO and AZO substrates (Fig.4b and 4c,  
165 respectively). More particularly, in the case of AZO coated substrate, voids are observed at  
166 the interface between CZTSe and AZO. The voids could be attributed to the reaction between  
167 Se and ZnO during the annealing to form the thin ZnSe layer and the emission of  $\text{SeO}_2$  gas in  
168 agreement with the Fig.2. Thus  $\text{SeO}_2$  diffusion into the CZTSe layer could degrades the  
169 interface.

170 The distribution of the chemical elements through the absorber layers deposited on Mo, FTO  
171 and AZO, obtained by GD-OES, are shown in Fig.5. For Mo and FTO coated substrates  
172 (Fig.5a and 5b, respectively), the profiles of Cu, Zn, Sn and Se are homogeneous throughout  
173 the thickness in agreement with the literature [13]. As observed in SEM pictures (Fig. 4d) the  
174 interface between CZTSe and FTO is rough. The interface roughness broadens the observed  
175 elemental profiles in GDOES. Moreover, as the Sn is both in the coating and in the substrate  
176 layer, it is not obvious to get a sharp interface between CZTSe and FTO and a gradual  
177 increase of Sn and O at the back side is observed while Cu, Zn and Se decreases. As shown by  
178 the thermodynamic calculations, FTO is quite stable at these temperatures confirming that the  
179 gradual increase of Sn and O at the CZTSe/FTO is not caused by the diffusion of Sn from  
180 FTO into CZTSe.



181 For the AZO coated substrate (Fig. 5c), the profiles of Cu and Sn appear relatively  
182 homogenous. However, the profiles of Zn and Se strongly vary through the thickness. Indeed,  
183 a segregation of Zn is visible at the back side. It seems that the composition of the substrate  
184 considerably modify the growth of CZTSe and especially its Zn content.

185 To highlight the impact of the AZO and FTO on the Na diffusion, the Na concentration in the  
186 CZTSe layer was also estimated by GD-OES. The standard Mo substrate allows the Na  
187 diffusion from the soda-lime glass to the CZTSe through the Mo layer. However the Na  
188 intensity for CZTSe on FTO and AZO back-contact are closed to 0, meaning that both FTO  
189 and AZO back-contacts hinder the diffusion of Na. The low diffusion of Na through TCO, in  
190 particular AZO and FTO has been evidenced on CIGSe based solar cells [8,27-29].

191 XRD patterns of CZTSe absorbers deposited on Mo, FTO and AZO are shown in Fig.6. The  
192 signature of Mo, FTO and AZO layers are visible. Moreover, the main reflections (112) at  
193  $27.29^\circ$ , (220) at  $45.28^\circ$ , and (312) at  $53.64^\circ$  of the CZTSe phase are clearly observed  
194 whatever the substrate [21]. For the Mo coated substrate, the SnSe<sub>2</sub> secondary phase (PDF  
195 089-3197) are also visible (Fig.6a) [30]. The (112) orientation of CZTSe is shown on a short  
196 range in the inset part of Fig.6. FWHM of (112) peak is sharper for CZTSe deposited on Mo  
197 and FTO than the one on AZO indicating a higher crystalline quality of CZTSe phase. These  
198 results are in agreement with the previous results in Fig.4 and 5 which show the disrupted  
199 growth of CZTSe deposited on AZO.

200 Due to the similar crystal structures of the ZnSe and Cu<sub>2</sub>SnSe<sub>3</sub> with CZTSe phases, it is not  
201 possible to conclude on the basis of X-ray measurements whether CZTSe if clearly formed.  
202 Thus, Raman spectroscopy is used to identify it. Raman spectra obtained with a 532 nm-laser  
203 wavelength of CZTSe films deposited on the different substrates Mo, FTO and AZO are  
204 shown in Fig.7a. Raman spectroscopy confirms the formation of the CZTSe phase on the  
205 different coated substrates.

206 It is important to note that even if SEM and XRD analysis have identified a thick ZnSe layer  
207 at the surface of AZO (Fig.2b, Fig. 3) after annealing, no ZnSe signal is observed for the  
208 CZTSe/AZO stack. In fact, the penetration depth of Raman spectroscopy is some hundreds of  
209 nanometers. Thus Raman spectroscopy cannot detect the signal of ZnSe at the interface  
210 between CZTSe and AZO.

211 Moreover, an additional peak attributed to the SnSe<sub>2</sub> phase is visible on the surface of CZTSe  
212 film deposited on FTO while it has not been detected by XRD. SnSe<sub>2</sub> is not a continuous film  
213 and could escape from the Raman and XRD analysis [30]. These complementary results show



214 that the SnSe<sub>2</sub> phase appears whatever the substrate and only depends on the growth  
215 conditions of CZTSe.

216 In order to access the interface between CZTSe and the TCO layer, lift-off technique has been  
217 used. However lift-off has been unsuccessful for CZTSe deposited on AZO. Fig.7b shows the  
218 Raman spectra of FTO coated substrate using UV laser wavelength after lift-off of CZTSe.  
219 FTO coated substrate before the CZTSe deposition is shown as reference. The FTO phase is  
220 observed and corresponds to the peak centered at 636 cm<sup>-1</sup> [31]. FTO coated substrate after  
221 lift-off reveals the presence of a secondary phase with 2 peaks at 568 cm<sup>-1</sup> and 1142 cm<sup>-1</sup>. This  
222 secondary phase fully absorbs UV laser wavelength and the peak of FTO centered at 636 cm<sup>-1</sup>  
223 is no longer visible. These 2 peaks are attributed to the 1st and 2nd order vibrations of the  
224 ZnO phase [32].

225 As Zn can be only provided by CZTSe layer, the ZnO phase at the interface between CZTSe  
226 and FTO could indicate the decomposition of CZTSe which provides the Cu, Zn and Sn  
227 elements. Thus the reaction of these elements with oxygen coming from FTO could product  
228 binary oxides. However, no additional secondary phases, such as Cu<sub>x</sub>O has been observed.

229 The formation of oxide secondary phases at the interface between chalcogenide and TCO has  
230 been observed in previous works. For example, for CIGSe films deposited on ITO, the  
231 presence of a Ga<sub>2</sub>O<sub>3</sub> resistive layer is reported [4,7] forming an electrical barrier for carrier  
232 transport [27,28]. For CZTSe films deposited on ITO, the formation of SnO<sub>2</sub> phases is  
233 reported. However, the effect of SnO<sub>2</sub> on the electrical properties of solar cells has been found  
234 negligible [12,18].

235 In order to assess the impact of the back contact on the electrical properties of solar cells IV  
236 measurements are performed on completed cells. Unfortunately all solar cells were shunted in  
237 the case of AZO/CZTSe based solar cells. In Fig.8.a, I-V curves for the best solar cells  
238 deposited on Mo/glass and FTO/glass substrates are reported. Their electrical parameters are  
239 summarized in Table 2. It can be found that all the electrical parameters of the solar cells  
240 deposited on FTO are lower than the ones deposited on Mo. For CZTSe absorbers deposited  
241 on Mo, the best solar cells have led to efficiencies up to 8.0 % [21,22]. The best efficiency of  
242 solar cells on FTO back contact is about 2.3%. The solar cells deposited on FTO suffer from a  
243 low FF, J<sub>sc</sub> and V<sub>oc</sub>. In fact, I-V characteristics under illumination of the solar cells deposited  
244 on FTO exhibits a slight slope at 0 V which shows that the solar cell has a current collection  
245 that depends on the voltage. The slope is higher under illumination than in the dark indicating  
246 the presence of recombination. It is well known that absence of Na is detrimental for the  
247 CZTSe cell (low doping concentration or high defect density), and the Na has to be supplied

248 by an external source. Moreover the back contact/CZTSe interface is the p-contact of the cell  
249 and has to be ohmic [19]. It has been shown that when the CZTSe is grown directly on FTO,  
250 an ohmic contact is achieved. However, the series resistances of the cells are slightly higher  
251 than the reference cells on Mo substrate. In our case a rectifying behavior is observed either  
252 due to the formation of a pn-junction between the n-type TCO and the p-type CZTSe or due to  
253 the high contact resistance of the ZnO secondary phase at the CZTS/SnO<sub>2</sub> interface. In fact  
254 ZnO is generally n-doped and therefore degrades the performance of the cell.

255 Fig.8b shows the EQE of the best solar cells deposited on Mo and FTO. The EQE spectrum  
256 exhibits a maximum around 560 nm at a level about 80% whatever the substrate. However,  
257 EQE drastically decreases with the wavelengths from 600 nm to 1200 nm for FTO coated  
258 substrate in contrary to Mo coated substrate. Integrated Jsc from EQE, obtained for the both  
259 solar cells, are 32.02 mA/cm<sup>2</sup> and 21.5 mA/cm<sup>2</sup> for CZTSe/Mo and CZTSe/FTO,  
260 respectively. These values are slightly higher than the ones obtained by I-V analysis. Low  
261 EQE is correlated with a low collection efficiency of the absorber, such as the losses at  
262 highest wavelengths in the near IR region could also be due to a recombination rate raised to  
263 the back contact [33,34]. Thus, several reasons can be reported to understand the low  
264 efficiency of CZTSe solar cell on FTO. On the one hand, in the case of Mo back contact, the  
265 formation of MoSe<sub>2</sub> at the CZTSe / Mo interface forms an ohmic contact. Thus, low  
266 recombination rate contributes to increase Voc, Jsc and FF. In the case of FTO back contact,  
267 high recombination rate comes from defects at the contact between CZTSe and FTO. In fact,  
268 ZnO secondary phases or diffusion of the oxygen to CZTSe could damage the interface. On  
269 the other hand, it has been observed that the TCO prevents the diffusion of Na through  
270 CZTSe. The diffusion of Na through CZTSe has a beneficial effect on doping concentration  
271 and defect density of the absorber. Thus, the improvement of the interface quality between  
272 CZTSe and FTO could also increase Voc and FF [28, 35-37].

273

#### 274 IV. Conclusion

275

276 CZTSe based solar cells deposited on Mo, ZnO:Al (AZO), and SnO<sub>2</sub>:F (FTO) coated  
277 substrate have been studied. It has been found that the annealing temperature under Se has no  
278 impact on the FTO substrate up to 600°C, whereas the temperature should remain below  
279 500°C for the 1300-nm-thick AZO. During the CZTSe deposition, FTO substrate is the most  
280 stable: no reaction are thermodynamically favored between the CZTSe phases and FTO.

281 However, CZTSe decomposition reaction is thermodynamically possible at the ZnO interface  
282 with the formation of a ZnSe phase. Moreover both FTO and AZO layer hinder the Na  
283 diffusion from the glass to the CZTSe absorbers leading to a lack of Na compared to the  
284 standard Mo substrate. Thus Solar cells based on CZTSe were made with an efficiency of  
285 2.3% on FTO while solar cells CZTSe deposited on Mo up to 8.0 %. Low efficiency of  
286 CZTSe solar cell on FTO coated substrate suffers of recombination at the back contact which  
287 limits Voc, Jsc and FF. Low efficiency has been explained by the presence of the ZnO  
288 secondary phase at the back contact and the low diffusion of Na through CZTSe.

289

292 [1] J. Kim, H. Hiroi, T. K. Todorov, O. Gunawan, M. Kuwahara, T. Gokmen, D. Nair, M.  
293 Hopstaken, B. Shin, Y. S. Lee, W. Wang, H. Sugimoto, et D. B. Mitzi, « High Efficiency  
294  $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$  Solar Cells by Applying a Double  $\text{In}_2\text{S}_3/\text{CdS}$  Emitter », *Adv. Mater.*, 26  
295 (2014) 7427- 7431.

296 [2] S. Temgoua, R. Bodeux, N. Naghavi, "A better understanding of the reaction pathways in  
297 the formation of  $\text{Cu}_2\text{ZnSn}(\text{S}_x,\text{Se}_{1-x})_4$  thin films", *Solar Energy Materials and Solar Cells*  
298 172 (2017) 160.

299 [3] S. Temgoua, R. Bodeux, N. Naghavi, "Influence of the annealing atmosphere and  
300 precursor's thickness on the properties of CZTSSe based solar cells" *Solar Energy Materials*  
301 *and Solar Cells* 191 (2019) 123-132

302 [4] T. Nakada, Y. Hirabayashi, T. Tokado, D. Ohmori and T. Mise, « Novel device structure  
303 for  $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$  thin film solar cells using transparent conducting oxide back and front  
304 contacts », *Sol. Energy*, 77, 6, (2004) 739- 747.

305 [5] D. L. Young, J. Abushama, R. Noufi, X. Li, J. Keane, T. A. Gessert, J. S. Ward, M.  
306 Contreras, M. Symko-Davies, and T. J. Coutts, "A new thin-film  $\text{CuGaSe}_2/\text{Cu}(\text{In},\text{Ga})\text{Se}_2$   
307 bifacial, tandem solar cell with both junctions formed simultaneously," in *Conference Record*  
308 *of the Twenty-Ninth IEEE Photovoltaic Specialists Conference*, 2002, pp. 608–611, May  
309 2002.

310 [6] S. Nishiwaki, S. Siebentritt, P. Walk, and M. Ch. Lux-Steiner, "A stacked chalcopyrite  
311 thin-film tandem solar cell with 1.2 V open-circuit voltage," *Progress in Photovoltaics :  
312 Research and Applications*, 11 (2003) 243–248.

313 [7] T. Nakada, "Microstructural and diffusion properties of CIGS thin film solar cells  
314 fabricated using transparent conducting oxide back contacts," *Thin Solid Films*, 480 (2005)  
315 419.

316 [8] F. Mollica, M. Jubault, F. Donsanti, A. Loubat, M. Bouttemy, A. Etcheberry, N. Naghavi,  
317 "Light management in ultra-thin CIGS solar cells by substituting the back contact with a  
318 TCO-based reflector", *Thin Solid films*, 633 (2017), 202-207.

- 319 [9] L. Gouillart, A. Cattoni, J. Goffard, F. Donsanti, G. Patriarche, M. Jubault, N. Naghavi, S.  
320 Collin "Development of reflective back contacts for high-efficiency ultrathin Cu(In,Ga)Se<sub>2</sub>  
321 solar cells", *Thin Solid Film* 672 (2019) 1–6.
- 322 [10] J. Ge, J. Chu, J. Jiang, Y. Yan, and P. Yang "Characteristics of In-Substituted CZTS Thin  
323 Film and Bifacial Solar Cell" *ACS Appl. Mater. Interfaces*, 6 (2014) 21118–21130.
- 324 [11] J. Ge, J. Chu, Y. Yan, J. Jiang and P. Yang, « Co-electroplated Kesterite Bifacial Thin-  
325 Film Solar Cells: A Study of Sulfurization Temperature », *ACS Appl. Mater. Interfaces*, 7  
326 (2015) 10414-10428.
- 327 [12] J. Ge, J. Chu, J. Jiang, Y. Yan, and P. Yang, "The Interfacial Reaction at ITO Back  
328 Contact in Kesterite CZTSSe Bifacial Solar Cells," *ACS Sustainable Chemistry &  
329 Engineering*, 3 (2015) 3043–3052.
- 330 [13] J.S. Kim, J.K. Kang, and D.K. Hwang, "High efficiency bifacial Cu<sub>2</sub>ZnSnSe<sub>4</sub> thin-film  
331 solar cells on transparent conducting oxide glass substrates", *APL Materials* 4 (2016) 096101.
- 332 [14] J.S. Kim, J.K. Kang and D.K. Hwanga, "Efficiency enhancement of bifacial Cu<sub>2</sub>ZnSnSe<sub>4</sub>  
333 thin-film solar cells on indium tin oxide glass substrates by suppressing In-Sn diffusion with  
334 Mo interlayer" *Journal of Power Sources* 400 (2018) 9–15.
- 335 [15] J. Ge, Y. Yu, W. Ke, J. Li, X. Tan, Z. Wang, J. Chu, and Y. Yan, "Improved Performance  
336 of Electroplated CZTS Thin-Film Solar Cells with Bifacial Configuration" *ChemSusChem*, 9  
337 (2016) 2149.
- 338 [16] P. K. Sarswat and M. L. Free, "Demonstration of a sol–gel synthesized bifacial CZTS  
339 photoelectrochemical cell," *physica status solidi (a)*, 208 (2011) 2861– 2864.
- 340 [17] P. K. Sarswat and M. L. Free, « A Comparative Study of Co-electrodeposited Cu<sub>2</sub>ZnSnS<sub>4</sub>  
341 Absorber Material on Fluorinated Tin Oxide and Molybdenum Substrates », *J. Electron.  
342 Mater.*, 41 (2012) 2210-2215.
- 343 [18] J. Henry, K. Mohanraj and G. Sivakumar, "Vacuum evaporated FTO/(Cu,Ag)<sub>2</sub>ZnSnSe<sub>4</sub>  
344 thin films and its electrochemical analysis", *Vacuum*, 160 (2019) 347-354.
- 345 [19] M. Espindola-Rodriguez, D. Sylla, Y. Sánchez, F. Oliva, S. Grini, M. Neuschitzer, L.  
346 Vines, V. Izquierdo-Roca, E. Saucedo, and M. Placidi, "Bifacial kesterite solar cells on FTO  
347 substrates" *ACS Sustainable Chem. Eng.* 2017, 5, 12, 11516-11524.
- 348 [20] D. Lee, "Solution-processed CZTS superstrate solar cell using vertically aligned

349 ZnO nanorods” *Nanotechnology*, 25 (2014) 065401.

350 [21] R. Bodeux, F. Mollica and S. Delbos, « Growth of  $\text{Cu}_2\text{ZnSnSe}_4$  by cosputtering and  
351 reactive annealing atmosphere », *Sol. Energy Mater. Sol. Cells*, 132 (2015) 6773.

352 [22] R. Bodeux, J. Rousset, F. Tsin, F. Mollica, E. Leite, S. Delbos, "Determination of the  
353 electronic properties of  $\text{Cu}_2\text{ZnSnSe}_4$  based solar cells by impedance spectroscopy and  
354 current–voltage characteristics analysis" *Applied Physics A* 124 (2018) 22.

355 [23] T. Olar, I. Lauermann, H. Xie, M. Neuschitzer, E. Saucedo, W. Calvet, A. Steigert, B.  
356 Ümsür, B. Chacko, V. Parvan, M. Gorgoi, B. Senkovskiy and M.L. Steiner," Assessment of  
357 chemical and electronic surface properties of the  $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$  after different etching  
358 procedures by synchrotron-based spectroscopies" *Energy Procedia* 84 (2015) 8 – 16.

359 [24] T. Tsirlina, “Growth of crystalline  $\text{WSe}_2$  and  $\text{WS}_2$  films on amorphous substrate by  
360 reactive (Van Der Waals) rheotaxy,” *Solar Energy Material & Solar Cells*, 44 (1996) 457.

361 [25] D. Lee and K. Yong, “Partial conversion reaction of ZnO nanowires to ZnSe by a simple  
362 selenization method and their photocatalytic activities,” *Materials Chemistry and Physics*,  
363 137 (2012) 194–199.

364 [26] F. Mollica, "Optimization of ultra-thin  $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$  based solar cells with alternative  
365 back-contacts" PhD thesis, University of Pierre et Marie Curie, France, 2016.

366 [27] F.-J. Haug, “Characterization of  $\text{CuGa}_2/\text{ZnO}$  for superstrate solar cells,” *Thin Solid*  
367 *Films*, 361 (2000) 293.

368 [28] F.-J. Haug, “Comparison of structural and electrical properties of  $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$  for  
369 superstrate and substrate solar cells,” *Thin Solid Films*, 403 (2002) 293.

370 [29] T. Prabhakar and N. Jampana, “Effect of sodium diffusion on the structural and electrical  
371 properties of  $\text{Cu}_2\text{ZnSnS}_4$  thin films” *Solar Energy Materials and Solar Cells*, 95 (2011) 1001-  
372 1004.

373 [30] S. Temgoua, R. Bodeux, N. Naghavi, et S. Delbos, « Effects of  $\text{SnSe}_2$  secondary phases  
374 on the efficiency of  $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$  based solar cells », *Thin Solid Films*, 582 (2015)  
375 215219.

376 [31] Z. W. Chen, J. K. L. Lai, and C. H. Shek, “Insights into microstructural evolution from  
377 nanocrystalline  $\text{SnO}_2$  thin films prepared by pulsed laser deposition,” *Physical Review B*, 70  
378 (2004) 165314.

- 379 [32] N. Xu, Y. Cui, Z. Hu, W. Yu, J. Sun, N. Xu, and J. Wu, “Photoluminescence and low-  
380 threshold lasing of ZnO nanorod arrays,” *Optics Express*, 20 (2012) 14857–14863.
- 381 [33] S. Siebentritt, “What limits the efficiency of chalcopyrite solar cells ?,” *Solar Energy*  
382 *Materials and Solar Cells*, 95 (2011) 1471–1476.
- 383 [34] L. Guo, Y. Zhu, O. Gunawan, T. Gokmen, V. R. Deline, S. Ahmed, L. T. Romankiw, and  
384 H. Deligianni, “Electrodeposited  $\text{Cu}_2\text{ZnSnSe}_4$  thin film solar cell with 7% power conversion  
385 efficiency,” *Progress in Photovoltaics : Research and Applications*, 22 (2014) 58-68.
- 386 [35] J. V. Li, D. Kuciauskas, M. R. Young, and I. L. Repins, “Effects of sodium incorporation  
387 in Co-evaporated  $\text{Cu}_2\text{ZnSnSe}_4$  thin-film solar cells,” *Applied Physics Letters*, 102, (2013)  
388 163905–163905–4.
- 389 [36] A. Nagaoka, H. Miyake, T. Taniyama, K. Kakimoto, Y. Nose, M. A. Scarpulla, and K.  
390 Yoshino, “Effects of sodium on electrical properties in  $\text{Cu}_2\text{ZnSnS}_4$  single crystal,” *Applied*  
391 *Physics Letters*, 104 (2014) 152101.
- 392 [37] T. Gershon, B. Shin, N. Bojarczuk, M. Hopstaken, D. B. Mitzi, and S. Guha, “The Role  
393 of Sodium as a Surfactant and Suppressor of Non-Radiative Recombination at Internal  
394 Surfaces in  $\text{Cu}_2\text{ZnSnS}_4$ ,” *Advanced Energy Materials*, 5 (2015) 1400849.



395

Table

396

397 **Table 1** Gibbs free energy of the potential reactions at the CZTS/back-contact.

Reaction equation	Gibbs free energy at 500°C Reaction equation per mol of Mo, ZnO or SnO <sub>2</sub> $\Delta G_f$ (kJ/mol)
$\text{Mo} + \text{Se}_2 = \text{MoSe}_2$	<b>-153</b>
$2\text{ZnO} + 1.5\text{Se}_2(\text{g}) = 2\text{ZnSe} + \text{SeO}_2(\text{g})$	<b>-30</b>
$\text{Cu}_2\text{Se} + \text{ZnO} = \text{Cu}_2\text{O} + \text{ZnSe}$	<b>87</b>
$\text{CuSe} + \text{ZnO} = \text{CuO} + \text{ZnSe}$	<b>63</b>
$\text{SnO}_2 + 1.5\text{Se}_2(\text{g}) = \text{SnSe}_2 + \text{SeO}_2(\text{g})$	<b>176</b>
$\text{SnO}_2 + \text{Se}_2(\text{g}) = \text{SnSe}(\text{g}) + \text{SeO}_2(\text{g})$	<b>286</b>
$2\text{Cu}_2\text{Se} + \text{SnO}_2 = 2\text{Cu}_2\text{O} + \text{SnSe}_2$	<b>287</b>
$2\text{CuSe} + \text{SnO}_2 = 2\text{CuO} + \text{SnSe}_2$	<b>241</b>

398

399 **Table 2** Electrical parameters of CZTSe based solar cells deposited on Mo/glass and

400 FTO/glass

	Voc (mV)	Jsc (mA/cm <sup>2</sup> )	FF (%)	Eff (%)	Eg (eV)
CZTSe/Mo	460	28.6	61	8.0	1.03
CZTSe/FTO	290	18.6	43	2.3	1.07

401

402

Figures

403

404

405 **Figure 1** Sheet resistances of AZO(500 nm), AZO(1300 nm), and FTO before and after  
406 annealing at different temperature under Se atmosphere for 45 min

407

408 **Figure 2** SEM morphologies of as deposited a) AZO, b) FTO and annealed c) AZO, d) FTO  
409 at 600°C for 45 min under Se atmosphere

410

411 **Figure 3** GIXRD patterns of a) FTO and b) AZO before and after annealing at 600°C under  
412 Se atmosphere for 45 min

413

414 **Figure 4** SEM morphologies of CZTSe absorber deposited on a), b) Mo, c),d) FTO et e),f)  
415 AZO

416

417 **Figure 5** GD-OES composition profiles for CZTSe deposited on a) Mo, b) FTO and c) AZO

418

419 **Figure 6** XRD patterns of CZTSe films deposited on Mo, AZO and FTO

420

421 **Figure 7** Raman spectra of a) CZTSe deposited on different substrates Mo, FTO and AZO at  
422 532 nm and b) FTO substrate at 325 nm laser wavelength before CZTSe deposition and after  
423 lifted off CZTSe

424

425 **Figure 8** J(V) curves of CZTSe based solar cells deposited on Mo/glass and FTO/glass

Figure 1  
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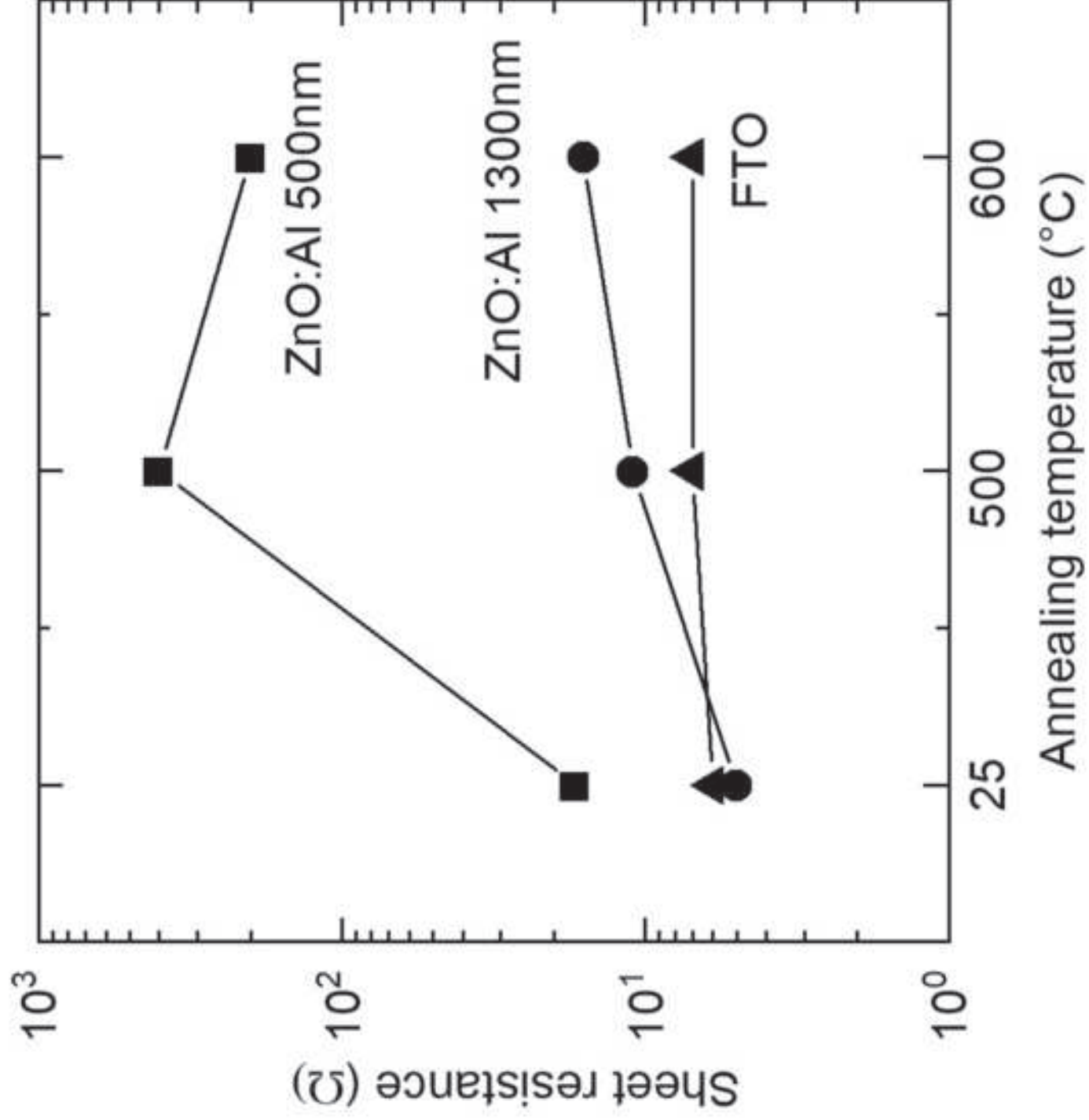


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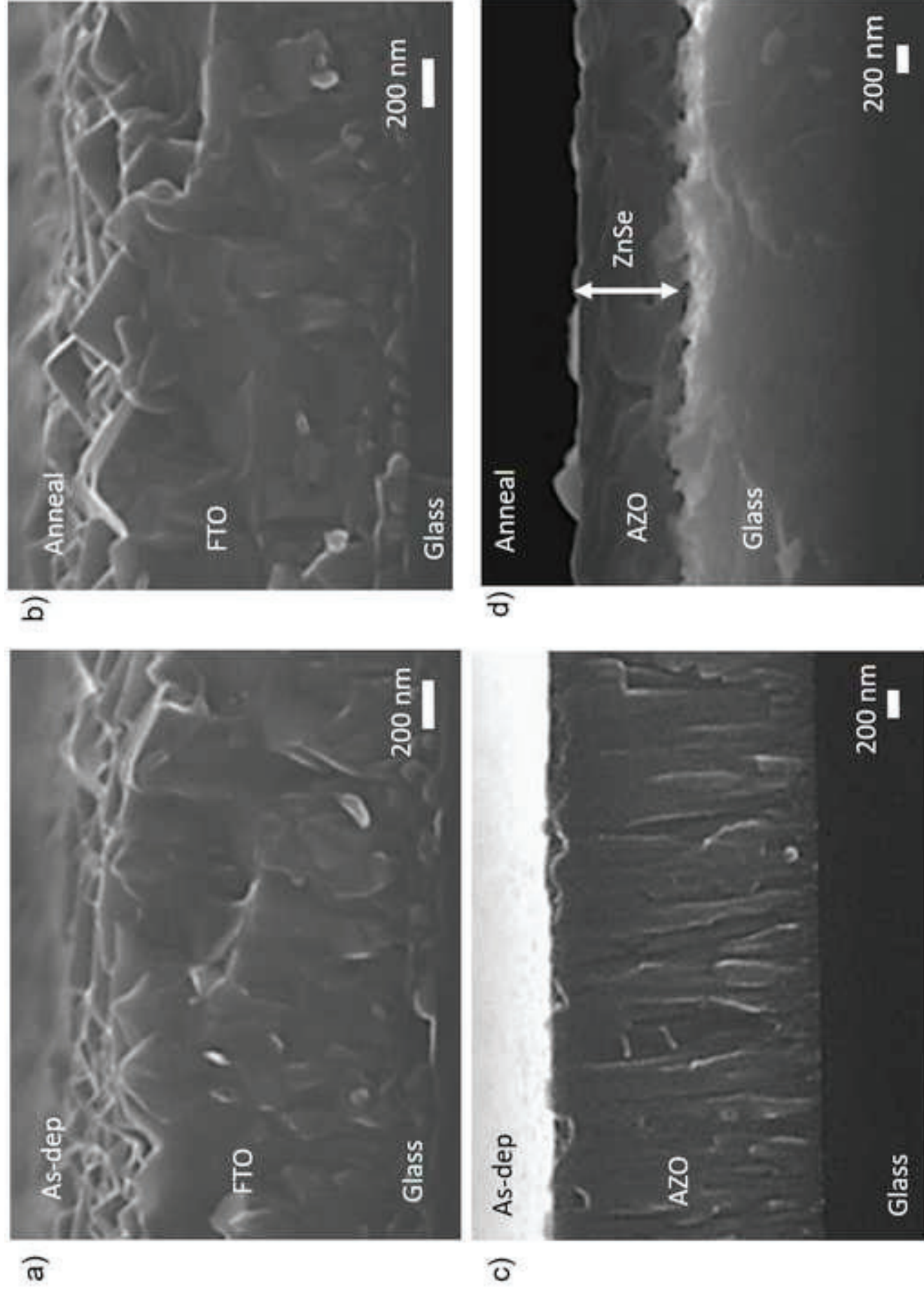


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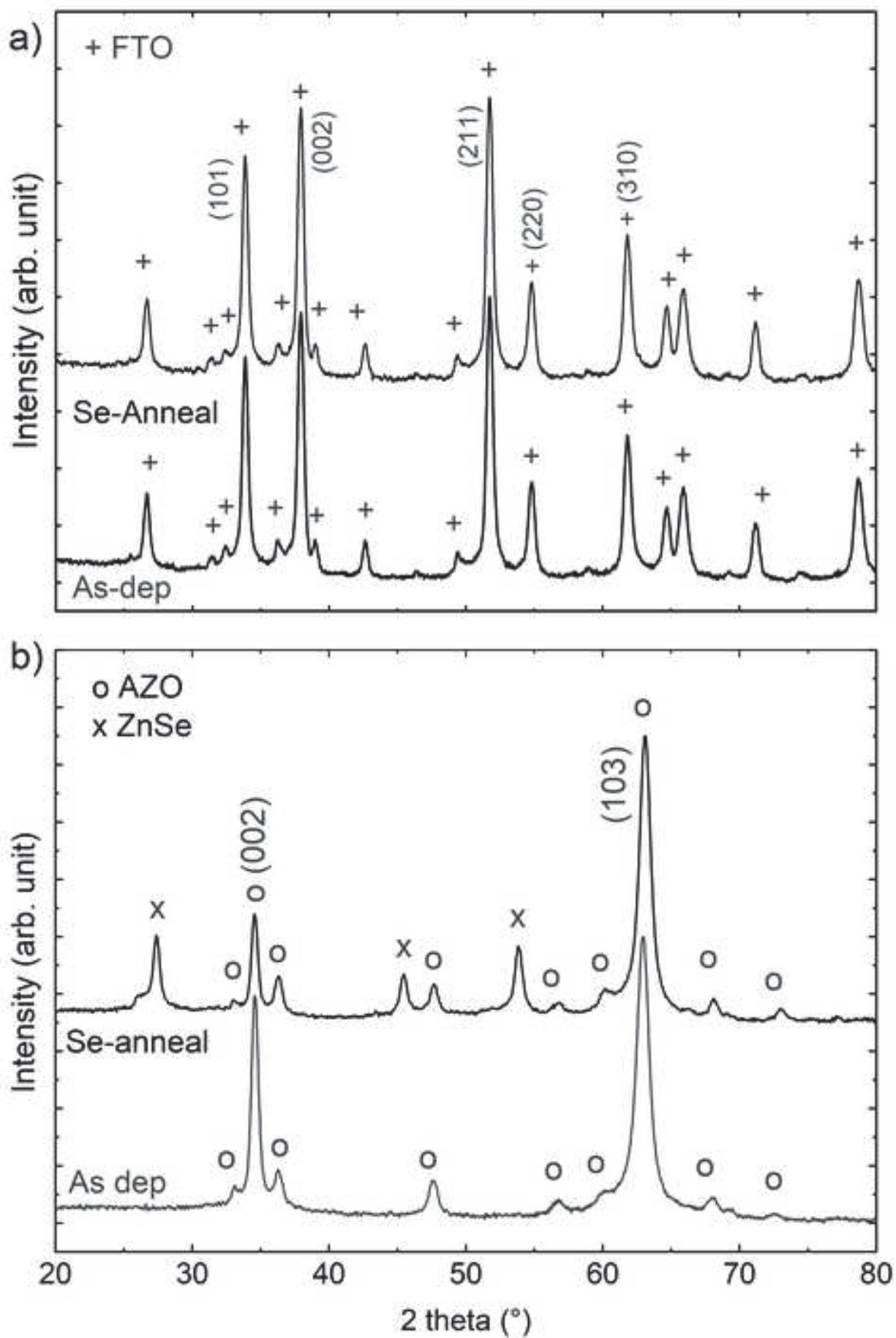




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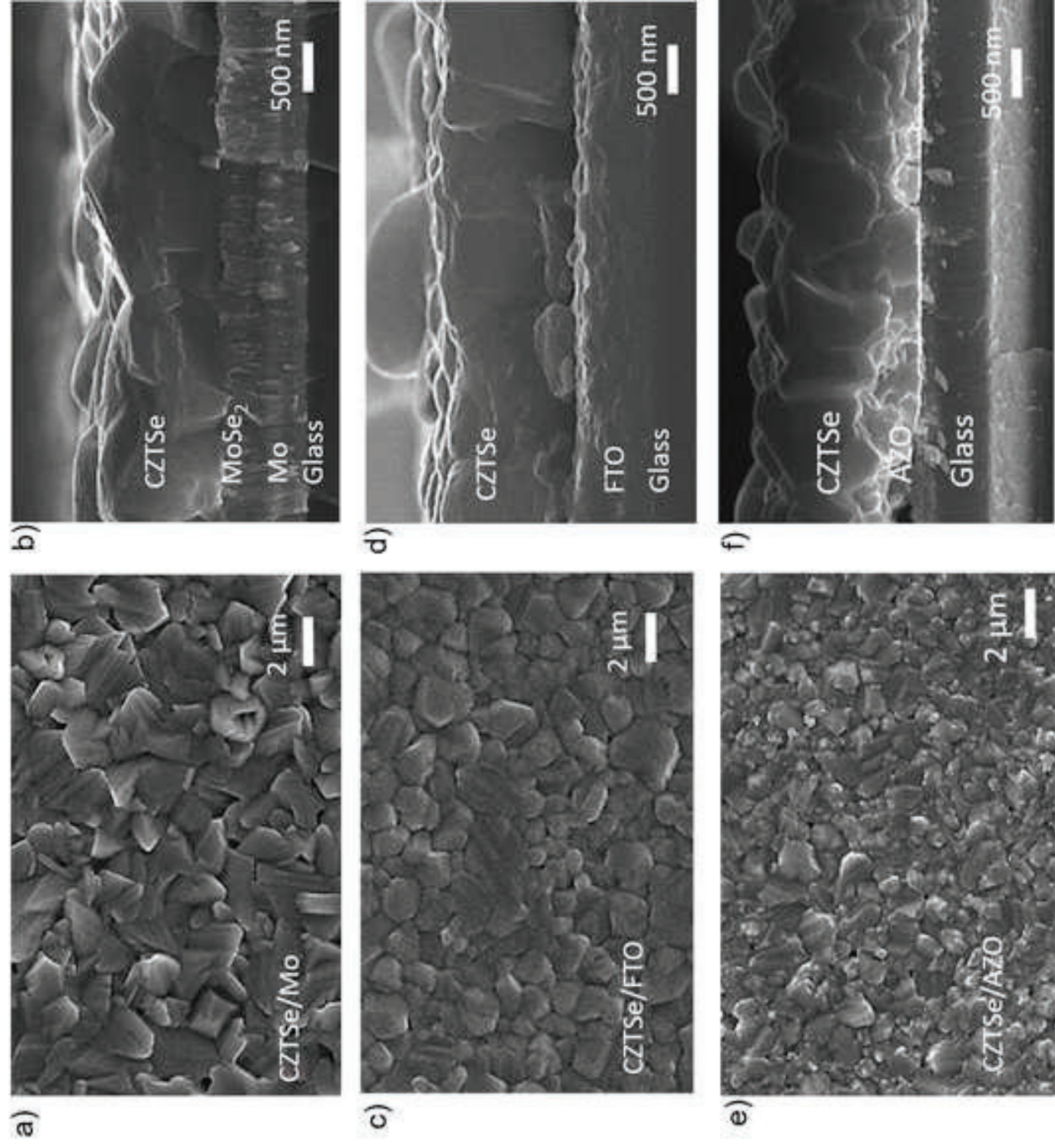


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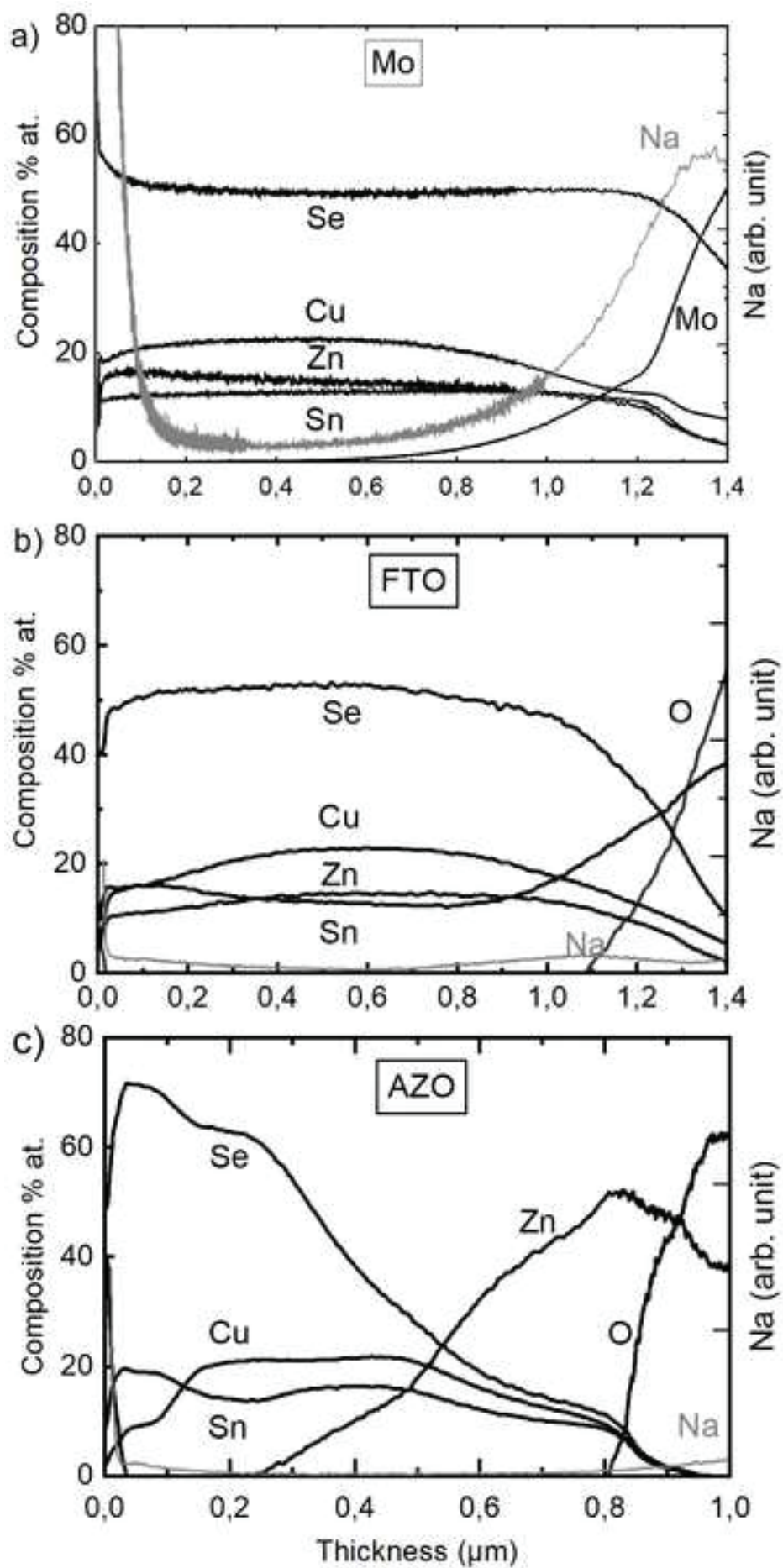




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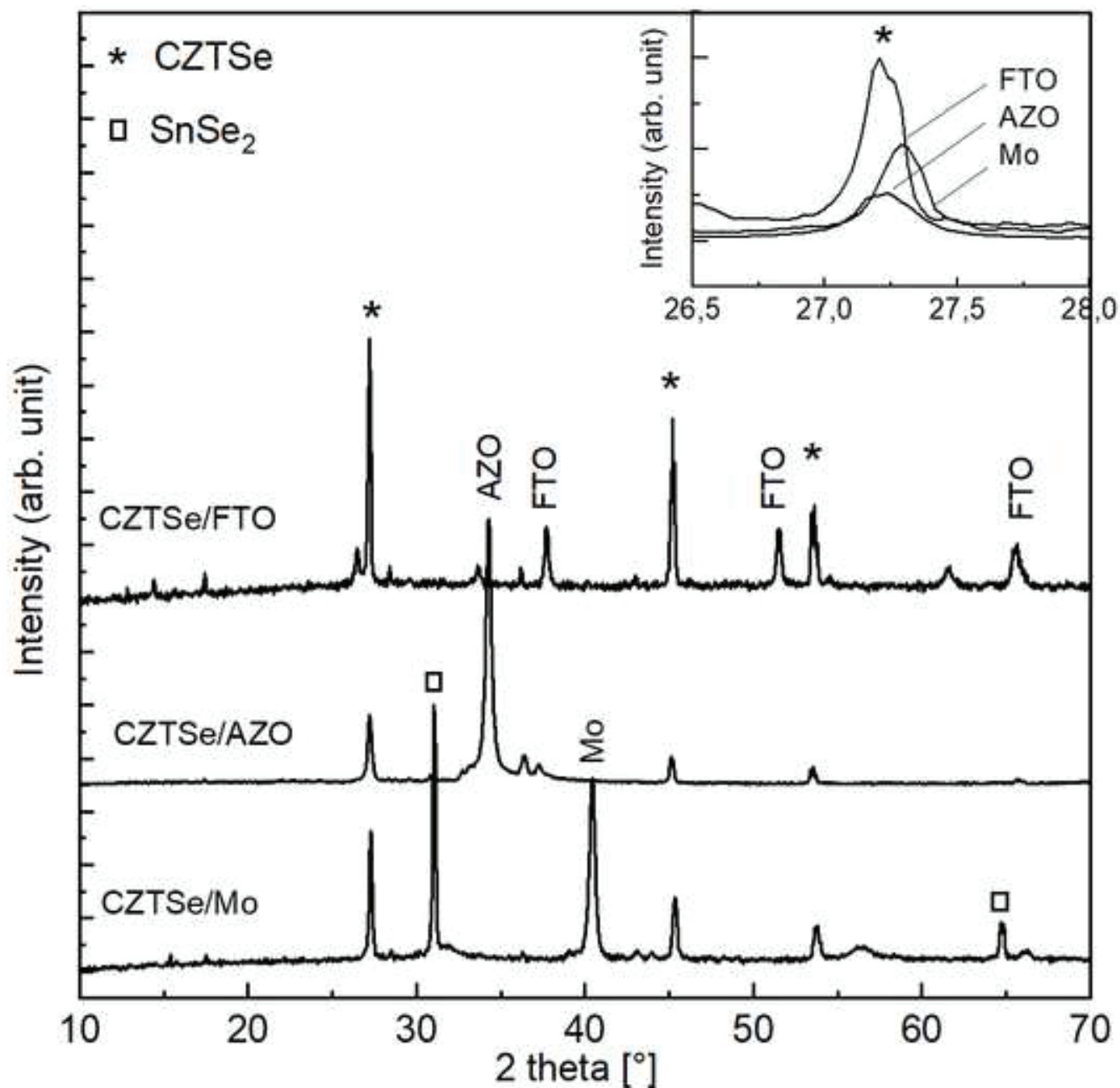


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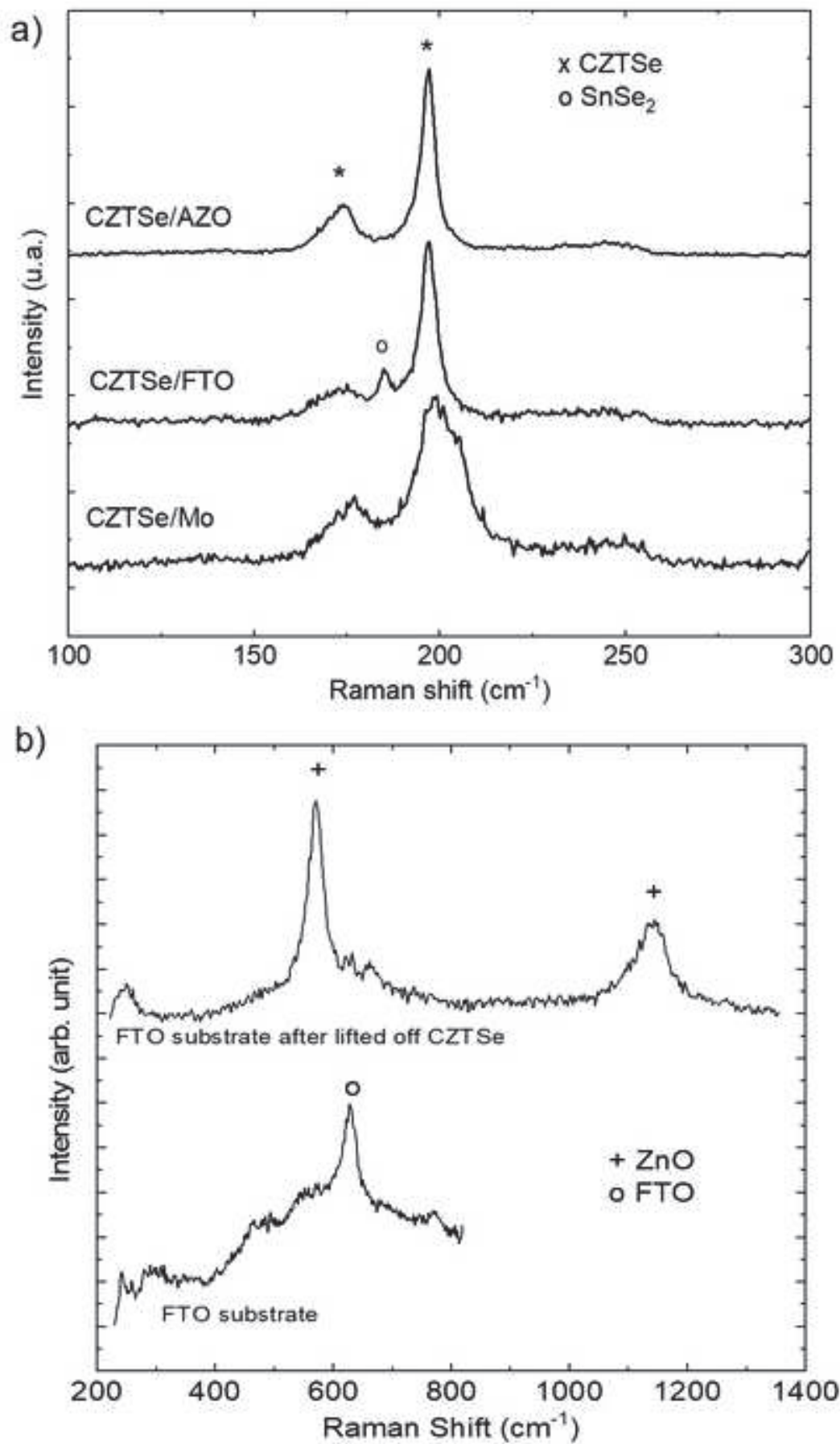


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