

1 **SUPPLEMENTARY MATERIAL FOR**

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3 **WIDE BAND GAP KESTERITE ABSORBERS FOR THIN FILM SOLAR CELLS:**

4 **POTENTIAL AND CHALLENGES FOR THEIR DEPLOYMENT IN TANDEM DEVICES**

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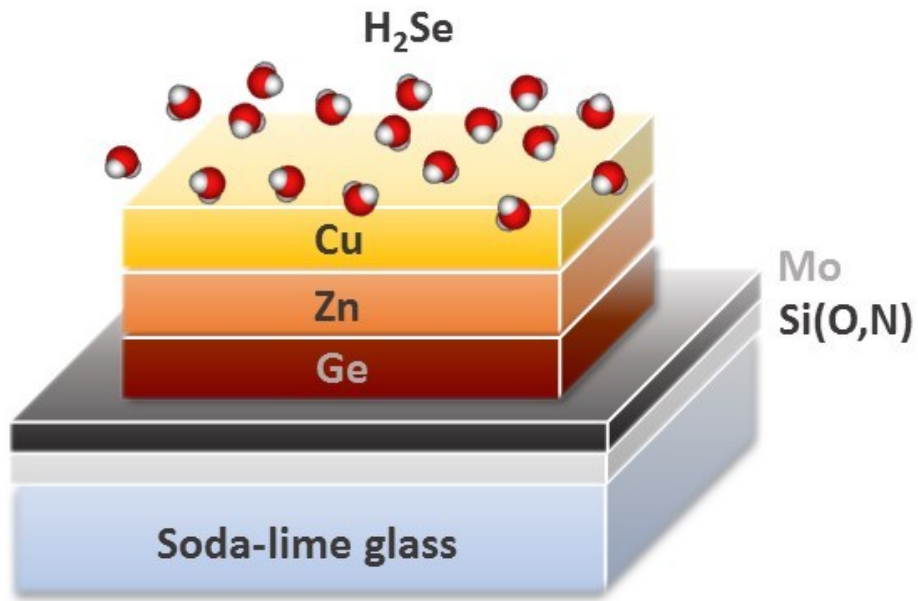
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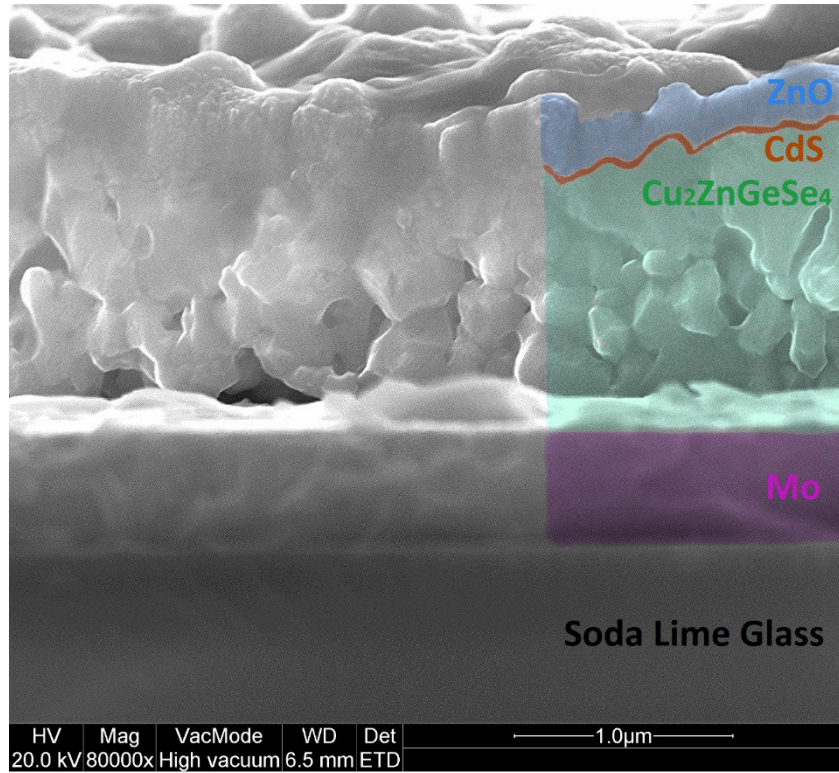
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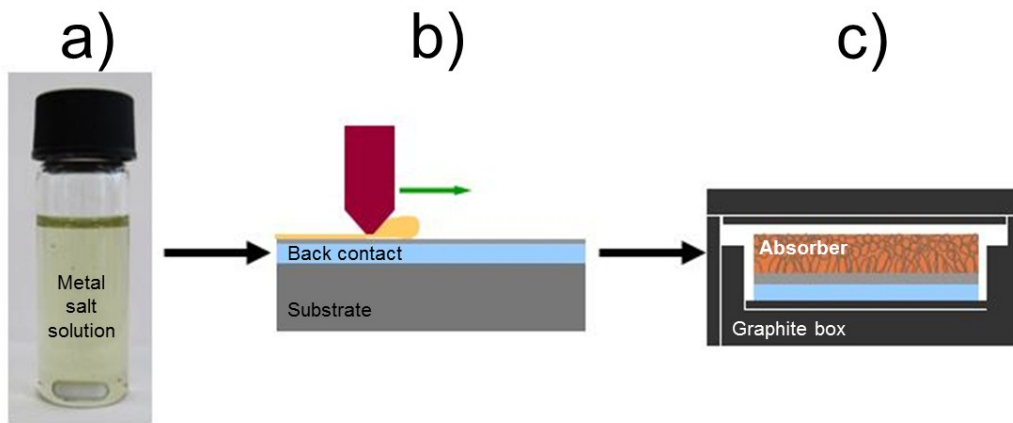
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Figure S1: Schematic representation of the two-step selenization process used for EVAP-Cu<sub>2</sub>ZnGeSe<sub>4</sub> absorber fabrication.



2 Figure S2: Cross-section scanning electron microscopy image of a finished EVAP-Cu<sub>2</sub>ZnGeSe<sub>4</sub>  
3 solar cell sample, showing the grain morphology of the absorber and contact layer.

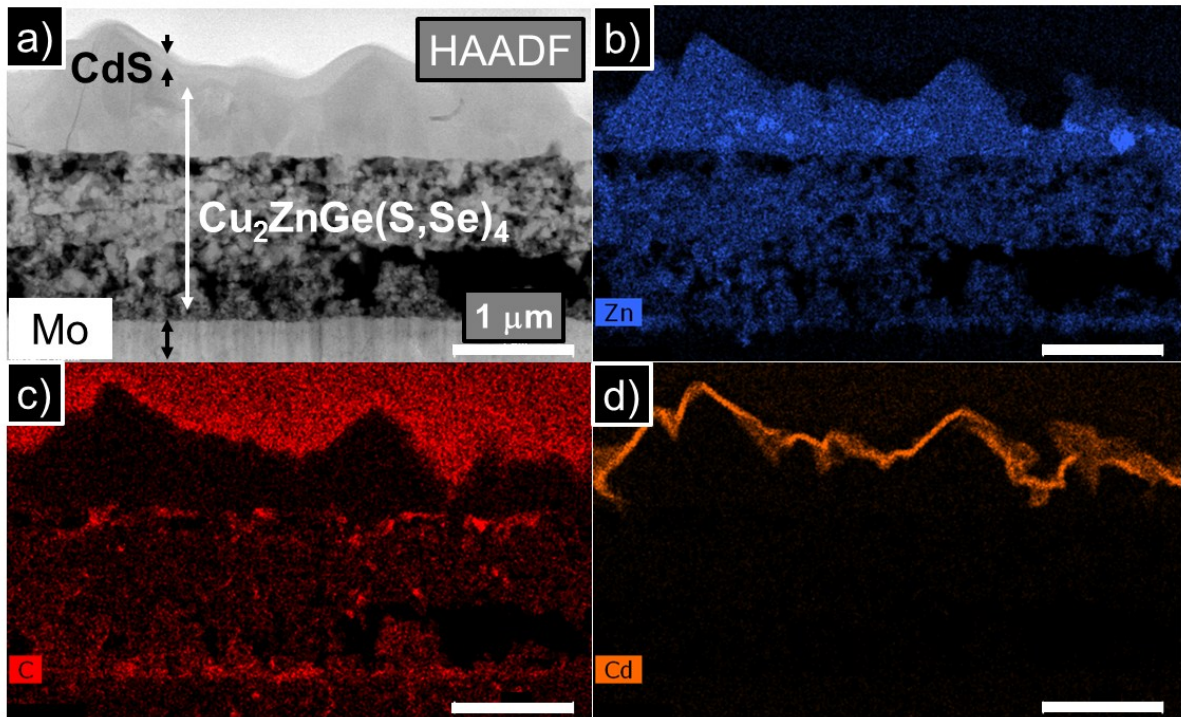
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2 Figure S3: Schematic illustration of the solution process of preparing a SOL-Cu<sub>2</sub>ZnGe(S,Se)<sub>4</sub>  
3 absorber: a) metal salt solution, b) doctor blade coating, c) annealing in Se atmosphere.

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2 Figure S4: Cross-section high angle annular dark field (HAADF) STEM image of a SOL-  
 3  $\text{Cu}_2\text{ZnGe}(\text{S},\text{Se})_4$ -based solar cell with CdS buffer and ZnO window (a), and the elemental  
 4 maps of Zn (b), C (c) and Cd (d).

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Buffer layer	$V_{oc}$ (mV)	FF (%)	$J_{sc}$ (mA/cm <sup>2</sup> )	$E_g$ (eV)	Eff. (%)
CBD CdS <sup>[17]</sup>	617	54.1	18.0	1.47	6.0
CBD Zn(O,S)	512	51.2	17.7	1.51	4.6
rf-Zn(O <sub>0.6</sub> S <sub>0.4</sub> ) <sup>[17]</sup>	730	48.3	13.0	1.54	4.6
ALCVD In <sub>2</sub> S <sub>3</sub> <sup>[17]</sup>	469	48.2	14.9	1.49-1.54	3.4
Co-evap. CdIn <sub>2</sub> S <sub>4</sub> <sup>[17]</sup>	354	49.6	14.7	1.44	2.6

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2 Table S1: Electrical parameters for the most efficient buffer/SOL-Cu<sub>2</sub>ZnGe(S,Se)<sub>4</sub> solar cells.

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Parameter	ZnO:Al	CdS	Cu <sub>2</sub> ZnGe(S,Se) <sub>4</sub>	MoSe <sub>2</sub> <sup>[31]</sup>	MoO <sub>3</sub> <sup>[32]</sup>
d (μm)	0.120	0.050	1-2	0.04-0.10	0.04
E <sub>G</sub> (eV)	3.3	2.4	1.47-1.5	1.1	2.85
χ (eV)	4.4	4.2	4.54	4.14	2.6
μ <sub>n</sub> (cm <sup>2</sup> /V.s)	100	100	10	100	100
μ <sub>p</sub> (cm <sup>2</sup> /V.s)	25	25	2	25	20
N <sub>d</sub> (cm <sup>-3</sup> )	10 <sup>18</sup>	3x10 <sup>17</sup>	-	-	-
N <sub>A</sub> (cm <sup>-3</sup> )	-	-	2x10 <sup>15</sup> / 10 <sup>16</sup> <sup>(0)</sup>	10 <sup>16</sup>	10 <sup>18</sup>
R <sub>s</sub> (Ω.cm <sup>-1</sup> )	4.7 / 0.5 <sup>(0)</sup>				
R <sub>sh</sub> (Ω.cm <sup>-1</sup> )	365 / 800 <sup>(0)</sup>				

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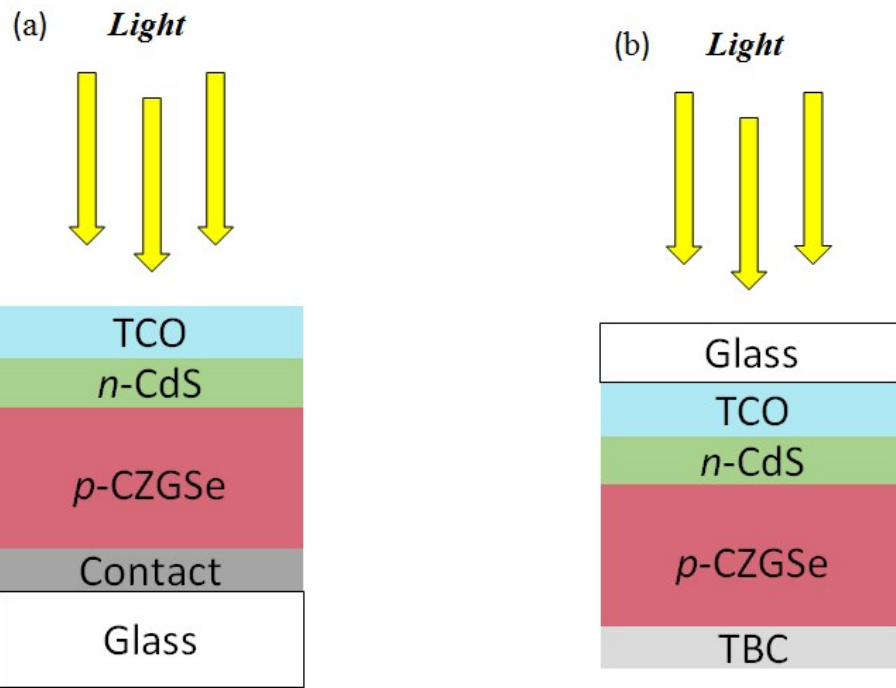
Table S2: Parameters used in the simulations at standard solar cell test conditions.

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<sup>(0)</sup> Optimized parameters.

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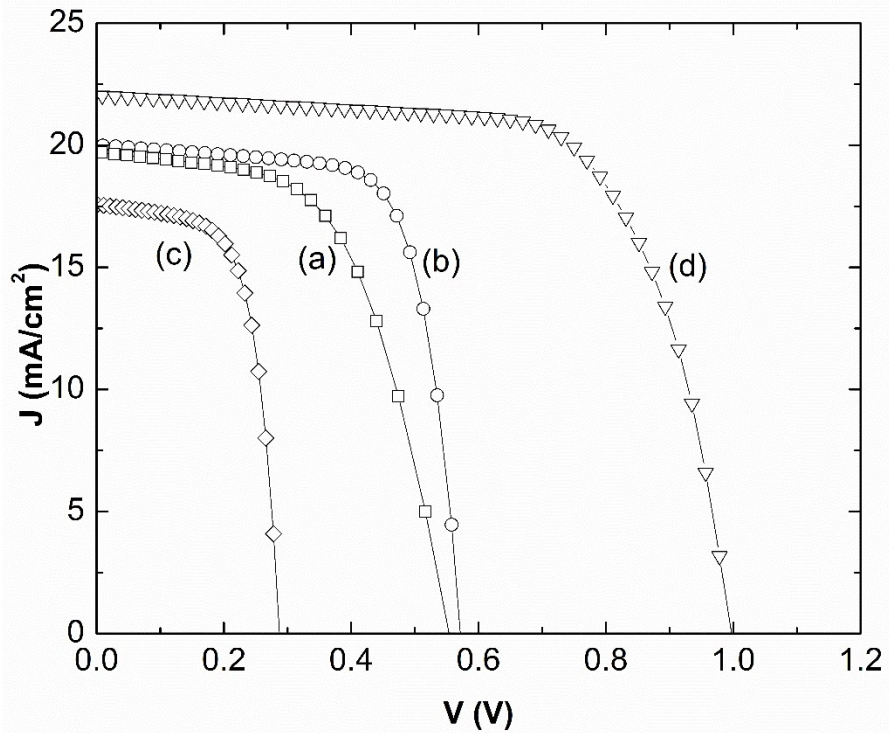
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Figure S5: Schematic of the two different configurations considered in the device simulations: (a) substrate and (b) superstrate.

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2 Figure S6: Calculated  $J(V)$  curves for different substrate/superstrate configurations: (a)  
 3 substrate =  $\text{Cu}_2\text{ZnGe}(\text{S},\text{Se})_4/\text{MoSe}_2/\text{Mo}/\text{glass}$ , (b) same configuration as (a) but using  
 4 optimized device simulation parameters (see Table S2), (c) superstrate =  
 5  $\text{Cu}_2\text{ZnGe}(\text{S},\text{Se})_4/\text{TCO}$ , and (d) superstrate =  $\text{Cu}_2\text{ZnGe}(\text{S},\text{Se})_4/\text{MoO}_3/\text{TCO}$ . For configurations (c)  
 6 and (d) also optimized parameters were used in the device simulation.

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