Supporting Information

Ag, Ti Dual-Cation Substitution in Cu₂ZnSn(S,Se)₄ Induced Growth

Promotion and Defects Suppression for High-Efficiency Solar Cells

Xing-Ye Chen^a, Muhammad Ishaq^a, Ahmad Nafees^a, Rong Tang^a, Zhuang-Hao Zheng^a, Ju-Guang Hu^a, Zheng-Hua Su^a, Ping Fan^a, Guang-Xing Liang^{a,*} and Shuo Chen^{a,*}



Figure S1. The statistic photovoltaic performances (V_{OC} , J_{SC} , FF and PCE) of CZTSSebased solar cells with various Ag substitution concentration.

(a)



Figure S2. SEM images of (a) Pristine, and (b) Ti substituted CZTSSe thin films.



Figure S3. The statistic photovoltaic performances (V_{OC} , J_{SC} , FF and PCE) of CZTSSebased solar cells with various Ti substitution concentration.



Figure S4. The statistic photovoltaic performances (V_{OC} , J_{SC} , FF and PCE) of 6%-Ag-substituted CZTSSe solar cells and various Ti substitution concentration.



Figure S5. (a) Dark *J-V* curves, and (b) Shunt conductance *G* characterizations of S-Ref, S-Ag and S-AgTi devices.

Device	Peak intensity (3d _{5/2})			Peak intensity (3d _{3/2})			
	Sn ⁴⁺	Sn ²⁺	total	Sn ⁴⁺	Sn ²⁺	Zn-Auger	total
S-Ref	135178	653169	788347	276652	327905	140982	745539
S-Ag	99822	624975	724797	228980	341544	109643	680167
S-AgTi	46474	509831	556305	129929	369864	59379	559172

Table S1. Fitting results of Sn 3d peaks of S-Ref, S-Ag and S-AgTi thin films



Figure S6. TEM image and TEM-coupled element mapping results for the champion S-AgTi device: (a) Cross-sectional TEM image, (b) Zn, and (c) Cd elemental mapping images.



Figure S7. EIS Nyquist plots of S-Ref, S-Ag, and S-AgTi devices. Inset is the equivalent circuit and the corresponding parameters.



Figure S8. UPS characterizations: secondary electron cut-off (SEC) edge and valence band (VB) position of S-Ref, S-Ag and S-AgTi thin films.