Supporting Information

Synthesis of simple, low cost and benign sol-gel $Cu_2In_xZn_{1-x}SnS_4$ alloy thin films: influence of different rapid thermal annealing condition and its photovoltaic solar cell

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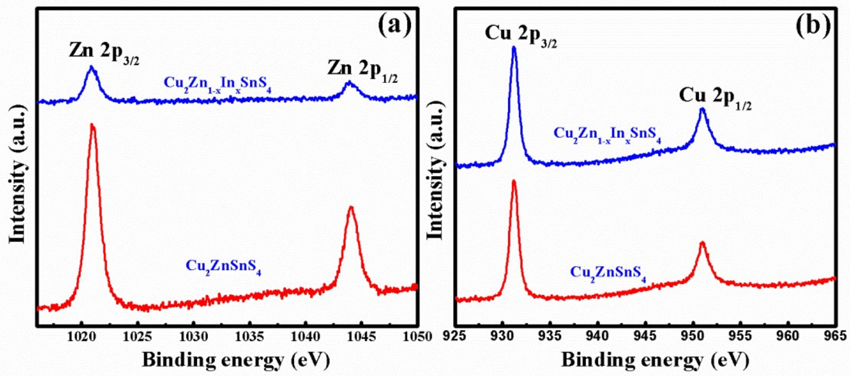

Fig. S1 The XPS spectra of (a) Zn 2p and (b) Cu 2p for CZTS and $Cu_2In_xZn_{1-x}SnS_4$ (x=0.4) thin films, respectively.

In the present work, to demonstrate that the Zn atom is exchanged with In for $Cu_2In_xZn_{1-x}SnS_4$ (x=0.4) alloy thin films, we have measured the XPS and Energy Dispersive Spectrometry (EDS) of the Cu_2ZnSnS_4 (CZTS) and $Cu_2In_xZn_{1-x}SnS_4$ (x=0.4) alloy thin films. The high-resolution scan XPS spectra of the Cu 2p and Zn 2p from the CZTS and $Cu_2In_xZn_{1-x}SnS_4$ (x=0.4) sample are shown in Fig. S1. The high-resolution scan XPS spectra of Zn 2p for the CZTS (x=0) and $Cu_2In_xZn_{1-x}SnS_4$ (x=0.4) sample are displayed in Fig. S1(a). Peaks at around 1020.7 and 1043.8 eV can be assigned to the Zn $2p_{3/2}$ and Zn $2p_{1/2}$, respectively, indicating that the Zn only exists in Zn^{2+}. Furthermore, the intensity of the Zn 2p peak decreases with the doping of the In, as shown in Fig. S1(a), implying that the relative content of the Zn decreases in the $Cu_2In_xZn_{1-x}SnS_4$ (x=0.4) film. The high-resolution scan XPS spectra of Cu 2p for the CZTS (x=0) and $Cu_2In_xZn_{1-x}SnS_4$ (x=0.4) sample are displayed in Fig. S1(b). Peaks at around 932.2 and 934.2 eV can be assigned to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively, with a spin–orbit splitting of 3.7 eV between $2p_{3/2}$ and $2p_{1/2}$, indicating that the Cu only exists in Cu^+. Furthermore, the intensity of the Cu 2p peak is almost constant with the doping of the In, as shown in Fig. S1(b). The increase of In content and almost constant Cu content indicate that In has been doped into the CZTS and occupied the sites of Zn atom in the CZTS crystal lattice.

Table S1 Summary of the EDS results of CZTS and $Cu_2In_xZn_{1-x}SnS_4$ (x=0.4) alloy thin films.

Sample	temperature(°C)	time(min)	Cu (at%)	Zn (at%)	Sn (at%)	In (at%)	S (at%)
CZTS	**580**	**60**	24.60	18.30	10.23	0	46.87
$Cu_2In_xZn_{1-x}SnS_4$	**580**	**60**	25.04	13.83	10.13	4.30	46.7

To further confirm that the Zn atom is exchanged with In. We also list the composition ratios of the Cu, Zn, Sn, In and S elements for the CZTS and $Cu_2In_xZn_{1-x}SnS_4$ (x=0.4) film in the Table S1. It is noted that the atomic percentage of Zn decreased with the increase of the In content in $Cu_2In_xZn_{1-x}SnS_4$ film. The Cu and anion contents remained relatively constant. It also very well support the conclusion about that the Zn atom is exchanged with In in $Cu_2In_xZn_{1-x}SnS_4$ film.

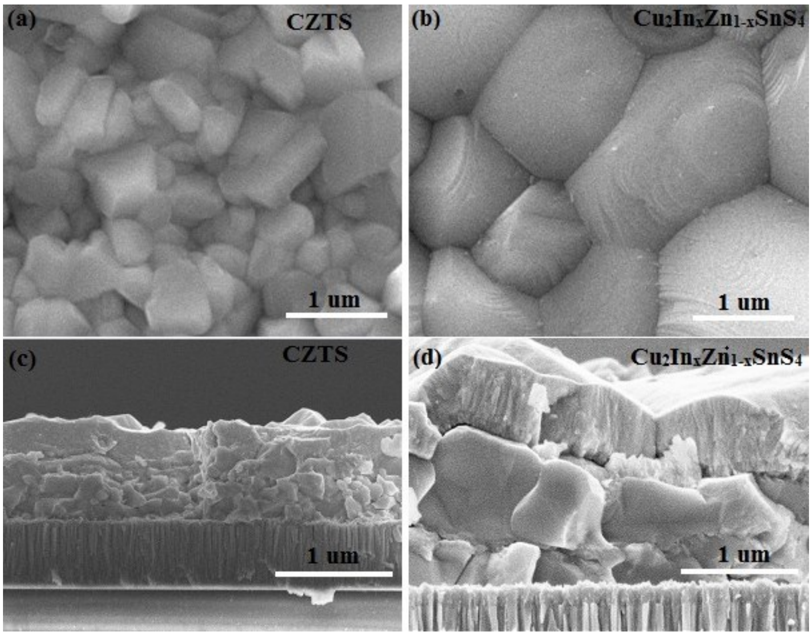

Fig. S2 The SEM images of (a) CZTS and (b) $Cu_2In_xZn_{1-x}SnS_4$ (x=0.4) thin films; the across-sectional SEM images of (c) CZTS and (d) $Cu_2In_xZn_{1-x}SnS_4$ (x=0.4) solar cells.

Fig. S2 displays the SEM images and across-sectional SEM images of the CZTS and $Cu_2In_xZn_{1-x}SnS_4$ (x=0.4) soalr cells. The SEM images and the across-sectional SEM images of the CZTS and $Cu_2In_xZn_{1-x}SnS_4$ (x=0.4) were shown in Fig. S2 (a-d). It was found from the Fig. S2 that the average grain size increases markedly after In doping.

Table S2 Summary of the EDS results of $Cu_2In_xZn_{1-x}SnS_4$ alloy thin film

Sample	Temperature (°C)	Time (min)	Cu (at%)	Zn (at%)	Sn (at%)	In (at%)	S (at%)	In/(In+Zn) (at%)
Cu_2ZnSnS_4	**580**	**60**	20.10	17.50	12.09	0	50.31	0
$Cu_2In_xZn_{1-x}SnS_4$	**580**	**60**	20.04	10.50	12.13	6.9	50.33	39

To understand whether In diffused into CdS layer, the elements ratios of CZTS and $Cu_2In_xZn_{1-x}SnS_4$ (x=0.4) absorber thin film for solar cells were measured by across-sectional SEM-EDS and are listed in Table S2. As shown in Table S2, the sum of In+Zn contents for $Cu_2In_xZn_{1-x}SnS_4$ (x=0.4) absorber are in agreement with the Zn contents of CZTS absorber. It indicated that In has been doped into the CZTS and occupied the sites of Zn atom in the CZTS crystal lattice. And it also indicated In did not diffused into CdS layer. This is probably because we did not have a subsequent annealing for solar cells after synthesizing the CdS layer.