Electronic Supporting Information

Nontoxic Solvent Based Sol-Gel Cu_2ZnSnS_4 Thin Film for High Efficiency and Scalable Low-cost Photovoltaic Cells

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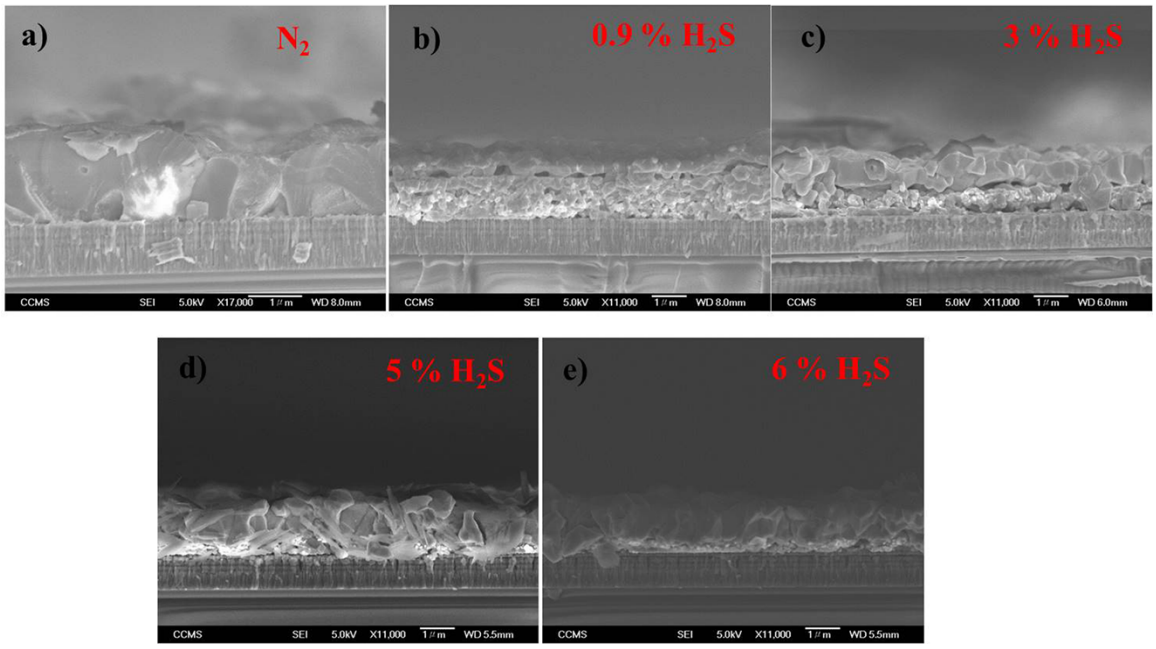

Fig.S1 CZTS thin films annealed at 610 ^oC for 8 minutes in various H_2S concentrations
a) In N_2 (0% H_2S concentration) b) 0.9% H_2S concentration c) 3% H_2S concentration d) 5% H_2S concentration e) 6% H_2S concentration

From the SEM images shown in **Figure S1a**, the grain size seems to be larger but the elemental composition analysis shows significant Sn loss from the film. The elemental distribution in the film from the top view EDS measurement yielded the Cu/(Zn+Sn) ratio to be 0.65±0.05, Zn/Sn ratio is 2.33±0.03 and S/metal ratio is 3.30±0.06.

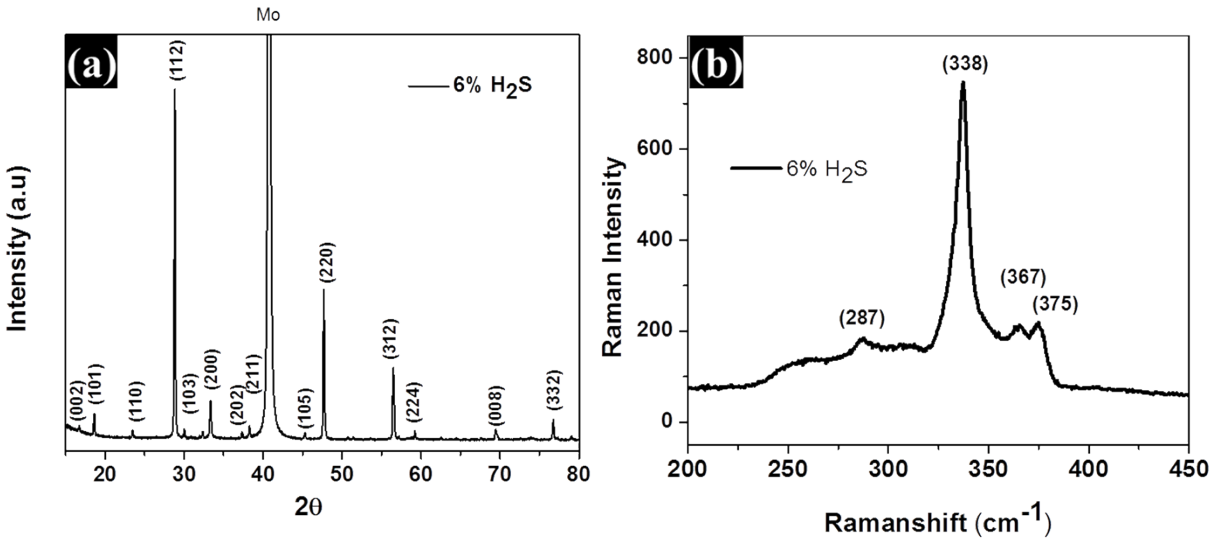

Fig.S2 a) Powder XRD diffraction pattern of CZTS thin film on Mo substrate annealed in 6% of H_2S environment b) Raman spectrum of CZTS thin film on Mo substrate annealed in 6% H_2S environment.

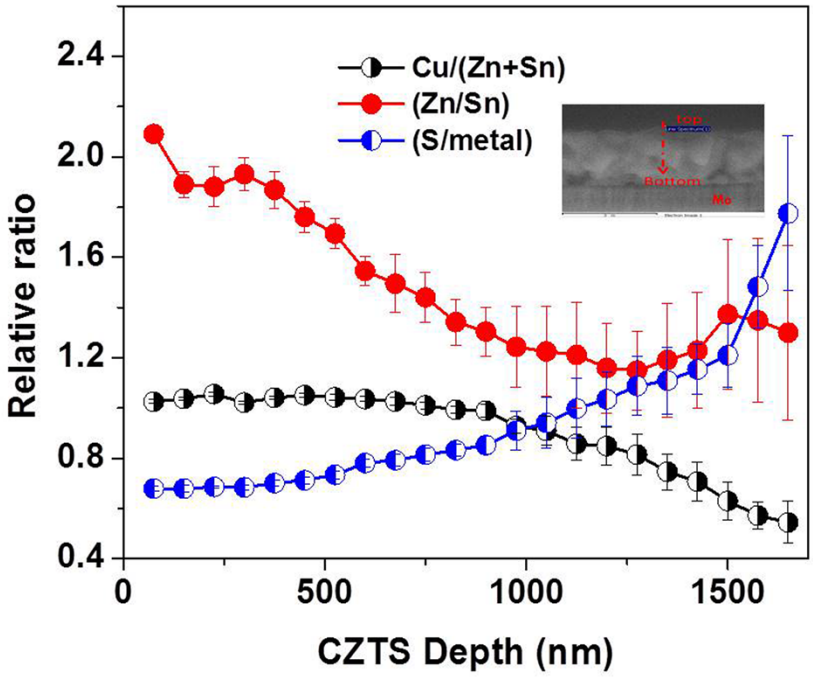

Fig.S3 Cross-sectional depth profile of CZTS thin film annealed in 6% H_2S environment

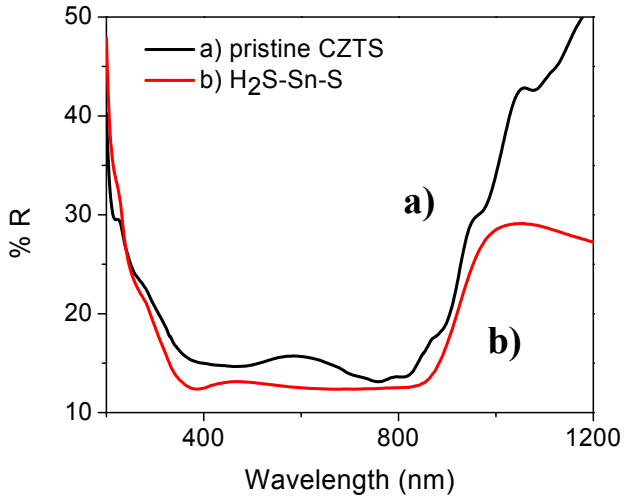

Fig.S4 UV-Visible spectrum of a) Pristine CZTS and b) CZTS annealed in 6% H_2S gas with externally provided Sn and Sulfur ambient

Fabrication of the device

Annealing profile

The pristine CZTS thin film was annealed under two conditions a) H_2S only, and b) Sn and S assisted annealing. The growth profiles are as shown in **Figure S4**

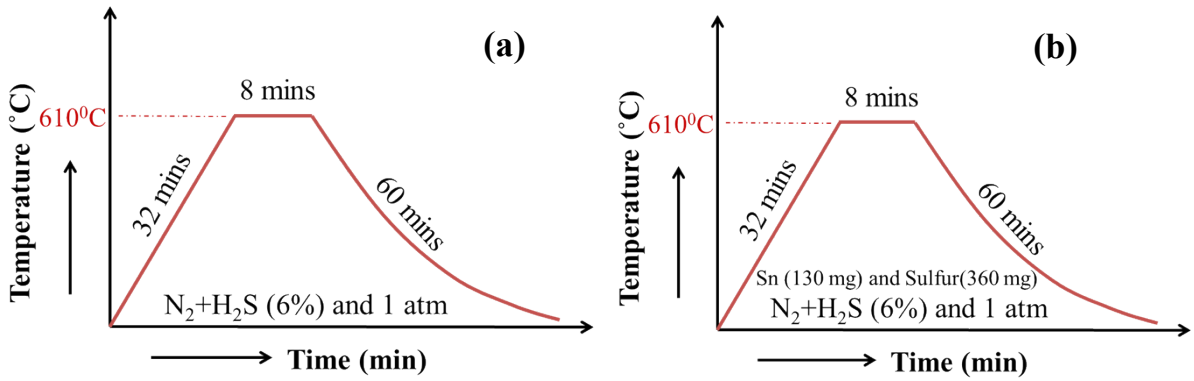

Fig.S5 Growth profiles of annealed CZTS thin films. a) H_2S only and b) modified-annealing

Cadmium Sulfide Deposition

0.0625 g of $CdSO_4$ was added to 78 mL deionized water, and 1.1418 g of thiourea was added to 100 mL deionized water separately. Both solutions were subjected to sonication until

the salts were completely dissolved. The SLG/Mo/CZTS samples to be coated with CdS were mounted on to CBD holder and immersed into $CdSO_4$ solution. The thiourea solution made as described above and 23 mL of ammonium hydroxide (35%) were mixed at room temperature and quickly placed into a pre-heated water bath at a temperature of 65 ^oC. The solution was continuously stirred at 45 rpm with a magnetic stir bar. After 15 min of coating, the samples were removed from the bath, rinsed with deionized water and dried under a nitrogen stream. The samples were then placed on a hot plate at 110 ^oC in air for 2 minutes.

RF sputtered window layer (i-ZnO) deposition

A 40 nm of i-ZnO window layer was RF sputtered on top of the SLG/Mo/CZTS/CdS (at 75 W RF power, 2 mTorr Ar pressure and 150˚C substrate temperature for 20 min)

DC sputtered Transparent Conducting Oxide layer (ITO) deposition

Following the window layer deposition, 350 nm of ITO (at 75 W DC power, 2 mTorr Ar pressure and 150 ^oC substrate temperature for 60 min) was DC sputtered on top of SLG/Mo/CZTS/CdS/i-ZnO. The sheet resistivity of the resulting ITO layer was approximately 80 ohms per square.

After the deposition of TCO layer, the entire device received a post heat treatment in air on hotplate at 200 ^oC for 10 minutes. The finished device was mechanically scribed with a knife to yield a device area of 0.15 cm^2.

Front contact

Silver (Ag) colloidal solution was used to make silver contacts as front electrode. The device was placed in air for at least 20 minutes to dry the solvent and solidify the Ag.