

Supporting Information

Chalcogenization-Derived Band Gap Grading in Solution-Processed $\text{CuIn}_x\text{Ga}_{1-x}(\text{Se,S})_2$ Thin-Film Solar Cells

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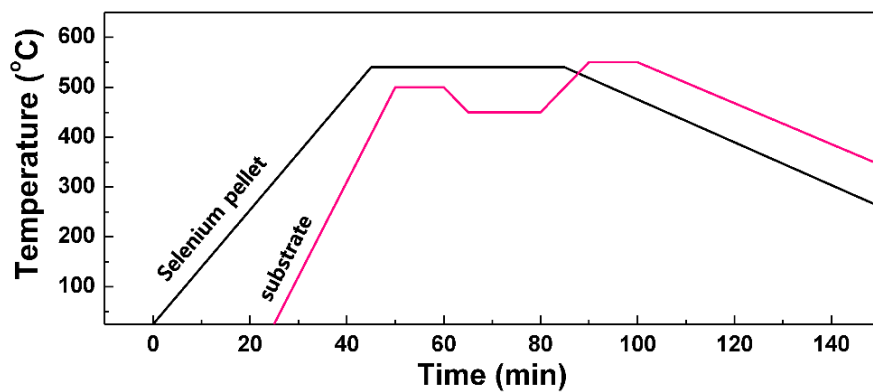


Figure S1. Temperature profiles of two zones of a tube furnace during selenization process.

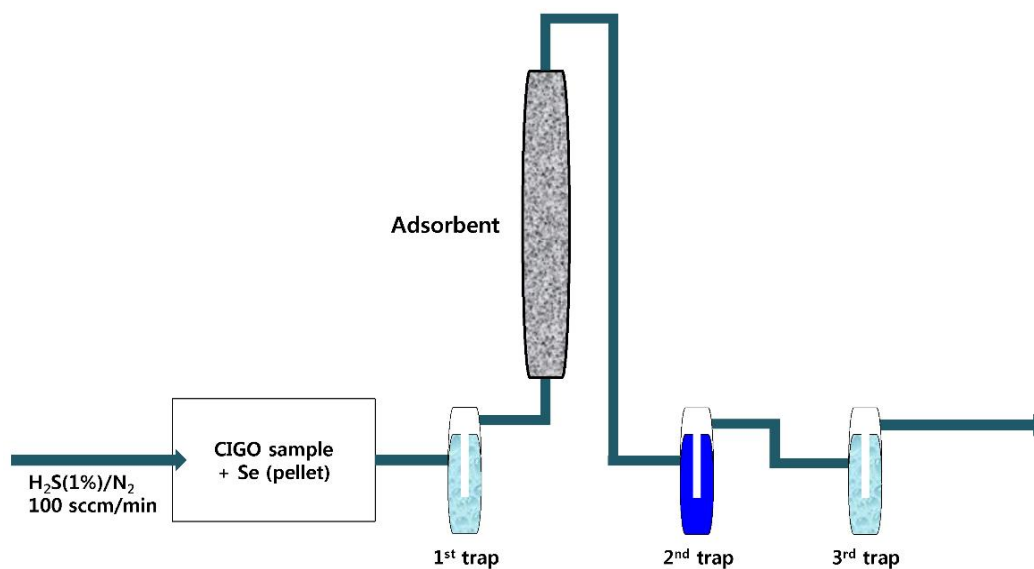


Figure S2. Schematic diagram of experimental setup for gas analysis and purification

For the synthesis of CIGSSe film, we attempted selenization under H_2S gas environment. In this process, H_2Se gas may be generated due to the reaction between H_2S and Se at high

temperature. H_2Se gas is a colorless and extremely toxic gas, thus requires caution and purification before releasing the gas to atmosphere. In order to check whether or not H_2Se gas is really generated, we prepared the setup as shown in Figure S2. First of all, the 1st trap with deionized (DI) water was connected to outlet of the reactor because H_2Se gas is soluble in water. Temperature of the trap was maintained at 4 °C because solubility of selenium in water is variable as temperature. Absorbent (PureSphere, Puresorb TA-301) was then connected to the outlet of the 1st trap to adsorb both H_2Se and H_2S gas. Sequentially, the 2nd trap with 0.1 M CuSO_4 in DI water was connected to the outlet of the absorbent, followed by installation of the 3rd trap of DI water to confirm the complete removal of H_2Se gas before releasing the gas to atmosphere through an exhaust gas hood. When residual H_2S gas was dissolved in CuSO_4 solution, a precipitate of CuS was formed due to the reaction: $\text{H}_2\text{S} (\text{g}) + \text{CuSO}_4 (\text{aq}) \rightarrow \text{CuS} (\text{s}) + \text{H}_2\text{SO}_4 (\text{aq})$.¹ Due to the black color of CuS precipitate, it is easy to confirm the ability of adsorbent. To quantify the generation of H_2Se gas the Se amount dissolved in the water trap was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) showing 30 ppm. To exclude any influence of Se vapor from a Se pallet on the quantification we tested with similar procedure under only N_2 gas without H_2S and no apparent Se in the 1st trap was detected by our ICP-OES. Notably, after passing the absorbent and the CuSO_4 solution trap no H_2S and H_2Se gas was dissolved in 3rd DI water trap indicating that our purification procedure is assumed to be reliable.

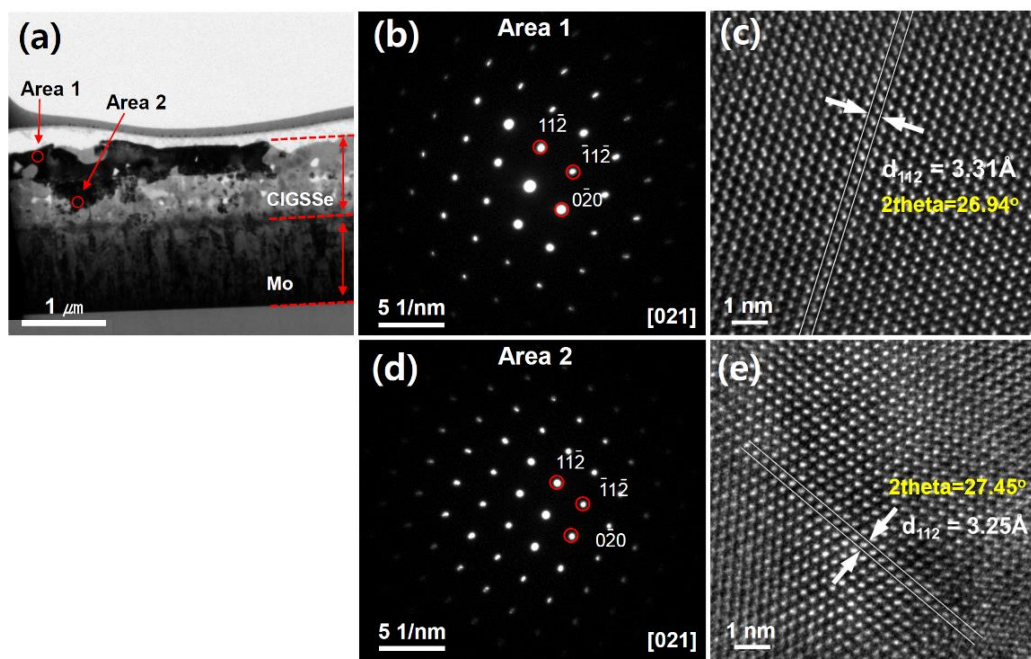


Figure S3. (a) Cross-sectional transmission electron microscopy (TEM) image of the CIGSSe film on Mo substrate, (b) and (d) selected area electron diffraction (SAED) patterns of the areas 1 and 2, and (c) and (e) high resolution TEM image of the selected area

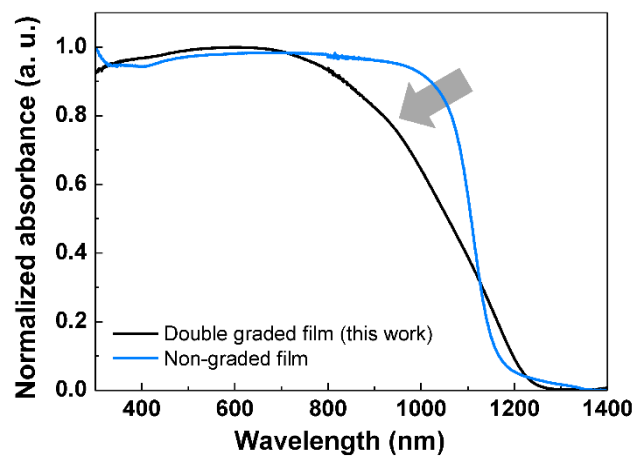


Figure S4. Comparison of absorption spectra of the double graded CIGSSe film and the non-graded CIGSSe film on glass substrate showing absorption loss of the double graded one (see an arrow).

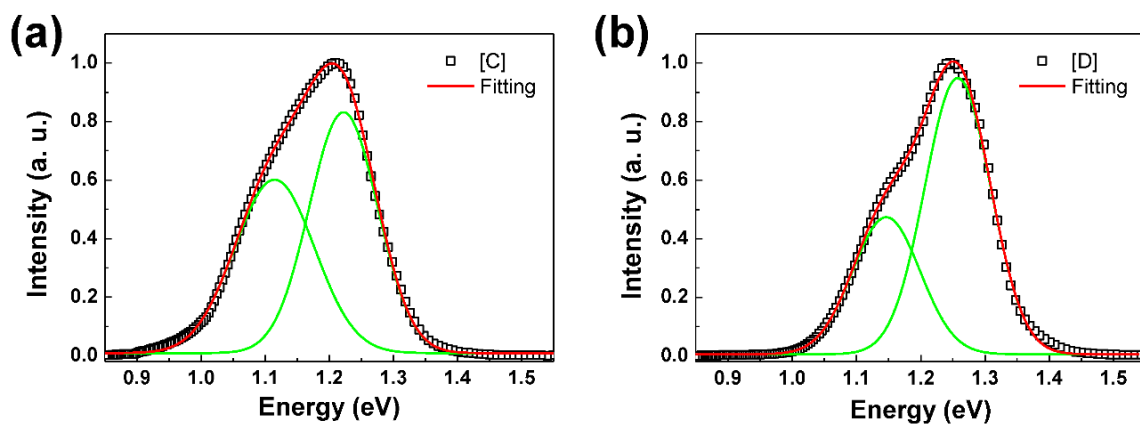


Figure S5. Photoluminescence (PL) spectra of (a) sample [C] and (b) sample [D] showed the wide and asymmetric shapes, which were deconvoluted by two Gaussian functions.

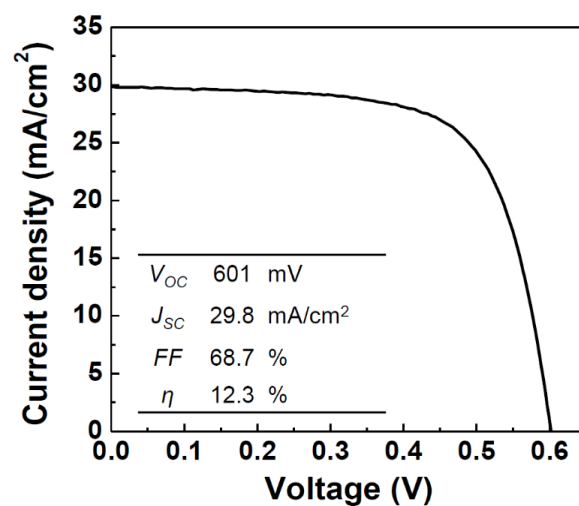


Figure S6. The current density-voltage (J - V) characteristics measured with an anti-reflection layer (MgF_2 , 100 nm) under simulated AM 1.5G illumination. The efficiency of the cells was calculated per active area (0.249 cm²).

Reference

- (1) Fergusson, J.; Hart, R. *CXC Chemistry*, Oxford University Press: Oxford, 1999.