Supporting Information

In-situ Al_2O_3 Incorporation Enhances the Efficiency of $CuIn(S,Se)_2$ Solar Cells Prepared from Molecular-Ink Solutions

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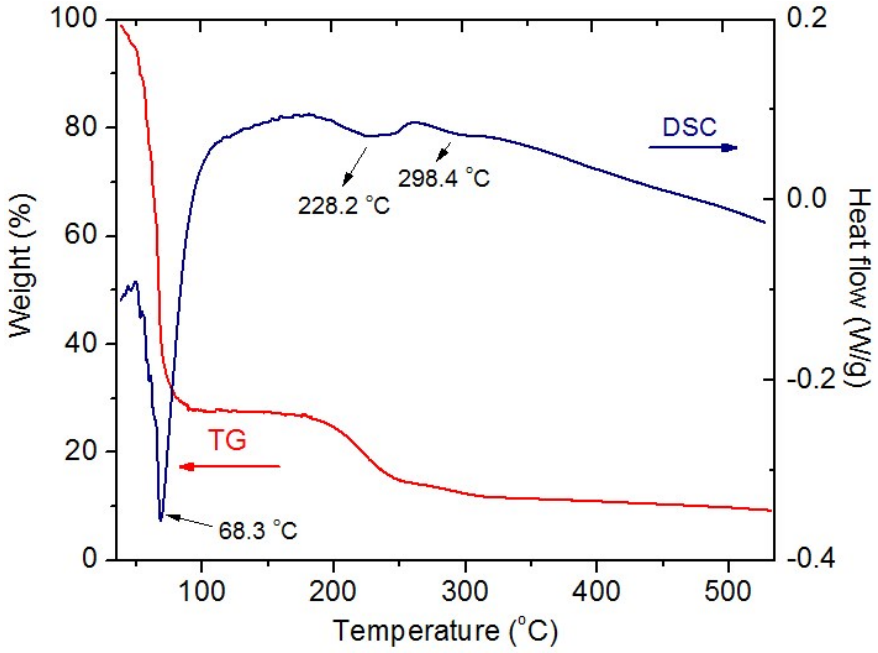

Figure S1. TG-DSC of ink made from CuCl-$InCl_3$-thiourea dissolved in methanol.

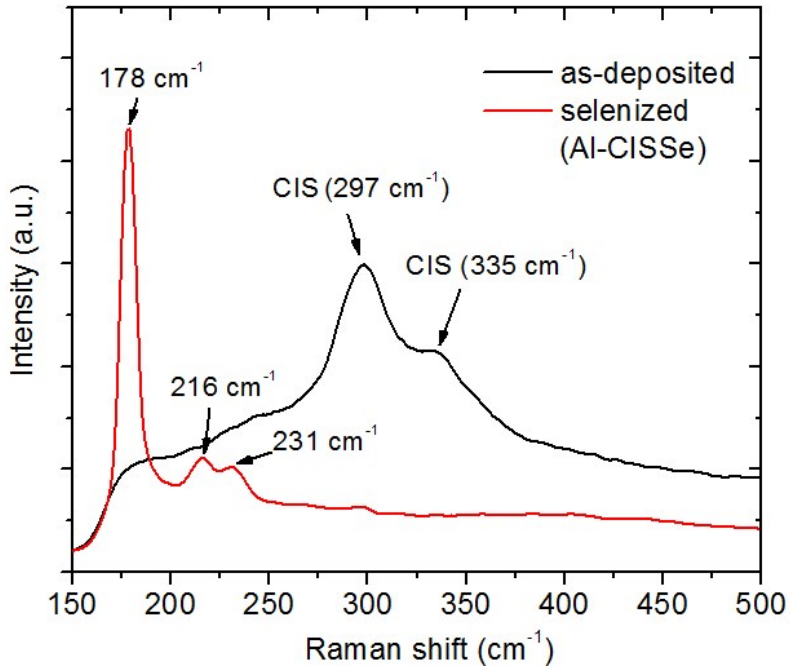

Figure S2. Raman spectra measured on as-deposited (Al-CIS) and selenized (Al-CISSe) films. The Raman spectrum of the Al-CISSe is identical to that of standard $CuInSe_2$, with a slight right-shift due to the presence of some sulfur in the film.[1]

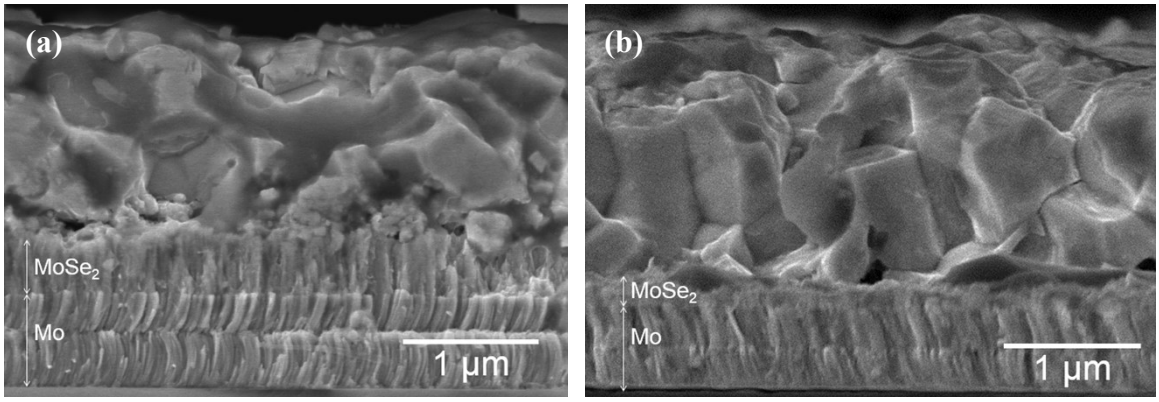

Figure S3. Secondary electron images of (a) Al-CISSe and (b) CISSe films.

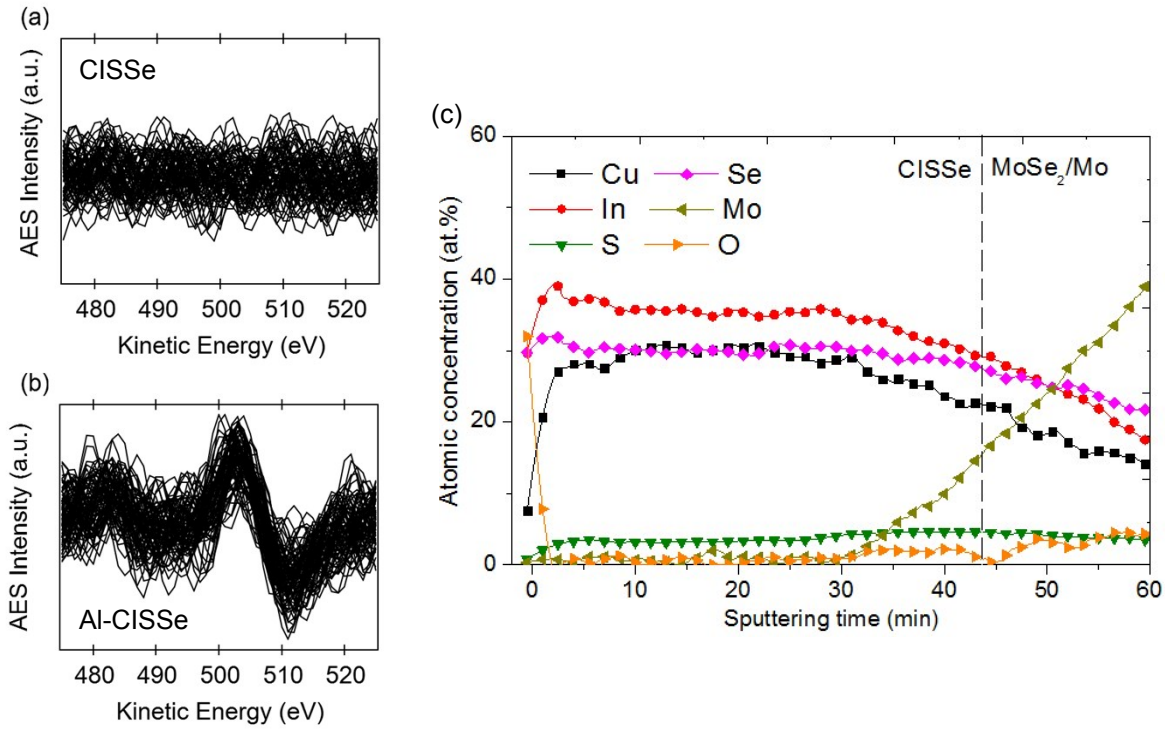

Figure S4. AES of oxygen region spectra taken from the bulk of (a) CISSe (72 spectra) and (b) Al-CISSe (83 spectra), excluding spectra from the interfaces (surface and Mo). (c) AES depth profiling of CISSe film.

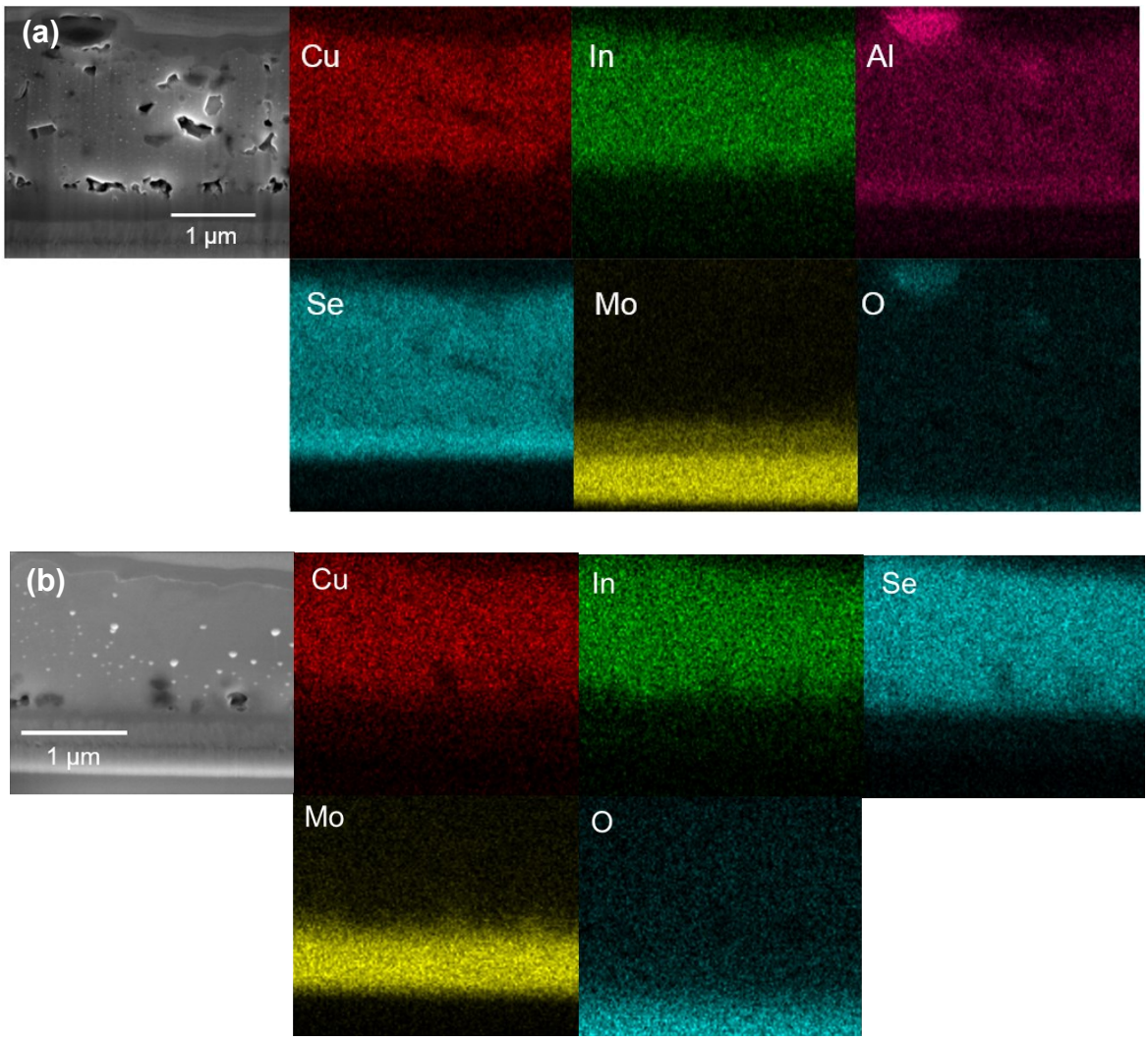

Figure S5. (a) SEM-EDX mapping across the Al-CISSe film where AlO_x segregates were observed on the surface of the film and inside the bulk. Characteristic X-ray energies of Al and Se exhibit some overlap (Al-Kα: 1.486 eV, Se-Lα: 1.379 eV), as a result, their apparent distributions in the maps show some mirroring with each other, and AES was used to determine composition. (b) SEM-EDX mapping of the CISSe film. Note that the white agglomerates observed in both SEM images of Al-CISSe and CISSe films are byproducts of the focused ion beam (FIB) process used to prepare the samples.[2]

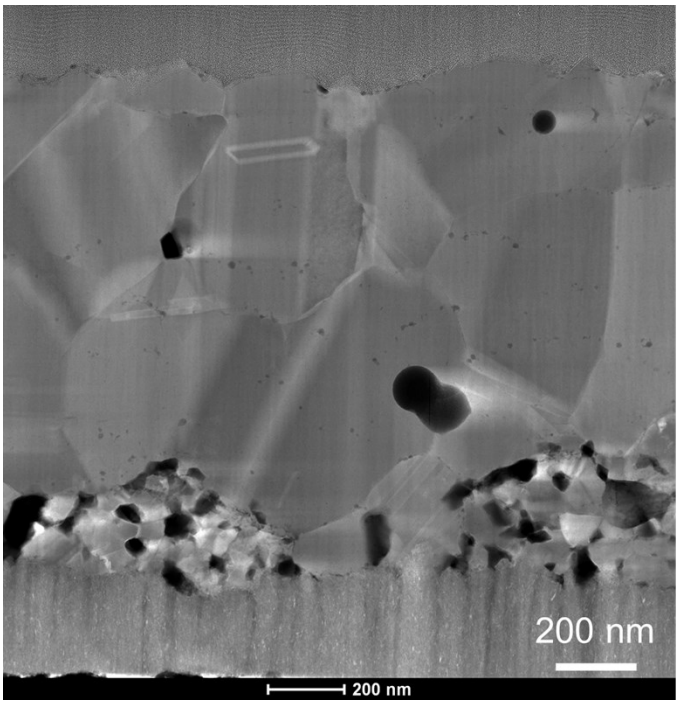

Figure S6. STEM high angle annular dark field (HAADF) image of Al-CISSe corresponding to the bright field image in Fig. 4a. Bright spots in Fig. 4a appear as dark in this image.

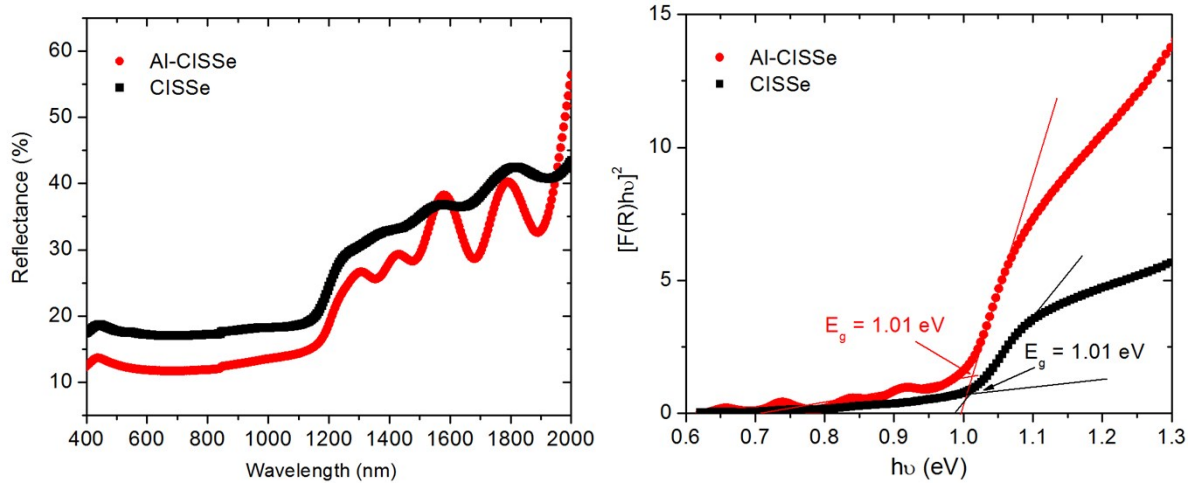

Figure S7. Diffuse reflectance spectrum of Al-CISSe and CISSe films and their Kubelka-Munk plots to estimate the optical band gaps.

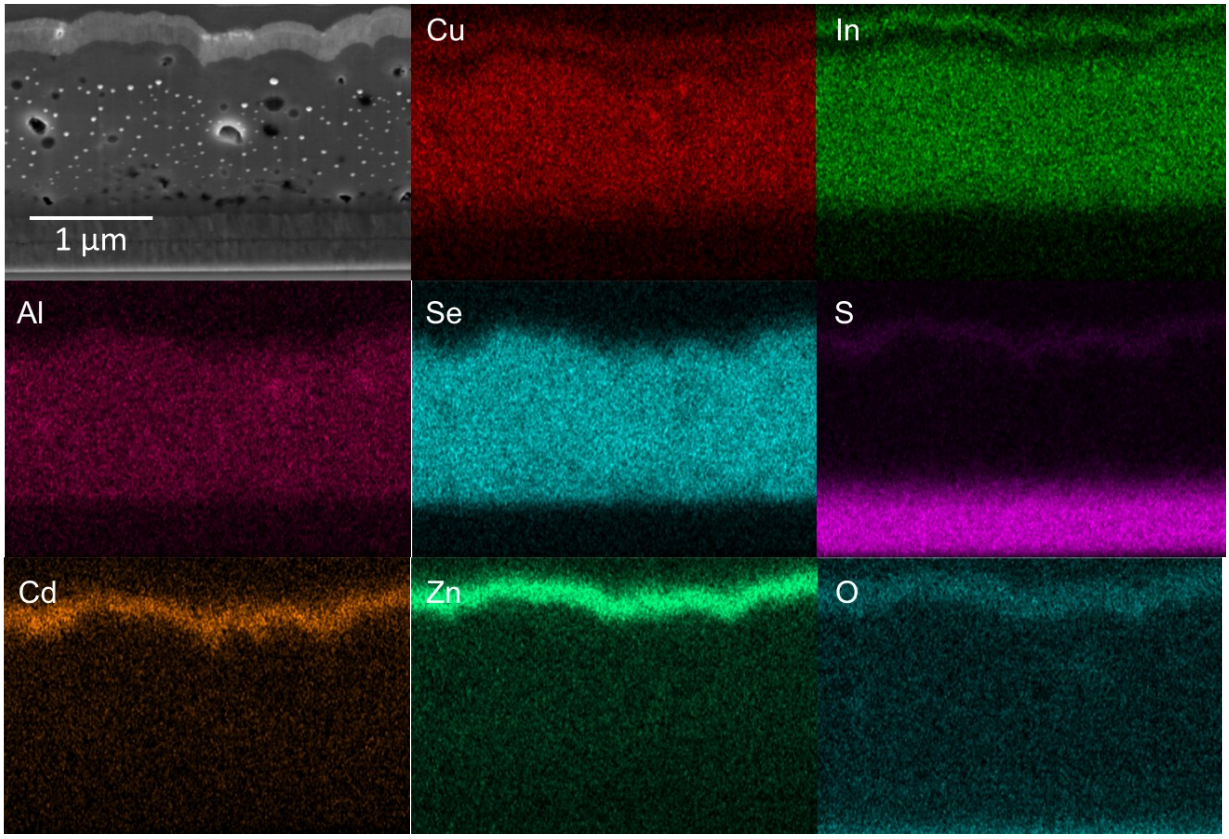

Figure S8. SEM-EDX mapping of Al-CISSe device (SLG/Mo/Al-CISSe/CdS/ZnO/ITO). Note that X-ray energies of Al and Se (Al-Kα: 1.486 eV, Se-Lα: 1.379 eV), Cu and Zn (Cu-Lα: 0.928 eV, Zn-Lα: 1.012 eV) exhibit some overlap. The white agglomerates observed in the SEM image are byproducts of the FIB process, as observed also in Figure S5.

References

[1] E.P. Zaretskaya, V.F. Gremenok, V. Riede, W. Schmitz, K. Bente, V.B. Zalesski and O.V. Ermakov, *J. Phys. Chem. Solids*, 2003, **64**, 1989.

[2] D. Abou-Ras, B. Marsen, T. Rissom, F. Frost, H. Schulz, F. Bauer, V. Efimova, V. Hoffmann and A. Eicke, *Micron*, 2012, **43**, 470.