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Defect control for 12.5% efficiency Cu2ZnSnSe4 kesterite thin-film solar cells by engineering of local chemical environment

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Abstract
Kesterite-based $Cu_2ZnSn(S,Se)_4$ semiconductors are emerging as promising materials for low-cost, environment-benign, and high-efficiency thin-film photovoltaics. However, the current state-of-the-art $Cu_2ZnSn(S,Se)_4$ devices suffer from cation-disordering defects and defect clusters, which generally result in severe potential fluctuation, low minority carrier lifetime, and ultimately unsatisfactory performance. Herein, we report critical growth conditions for obtaining high-quality $Cu_2ZnSnSe_4$ absorber layers with the formation of detrimental intrinsic defects largely suppressed. By controlling the oxidation states of cations and modifying the local chemical composition, we essentially modify the local chemical environment during the synthesis of kesterite phase, thereby effectively suppressing detrimental intrinsic defects and activating desirable shallow acceptor Cu vacancies. Consequently, we demonstrate a confirmed 12.5% efficiency with high VOC of 491 mV and greatly reduced VOC deficit. These encouraging results demonstrate an essential route to overcome the long-standing challenge of defect control in kesterite semiconductors, which may also be generally applicable to other multinary compound semiconductors.

High lights:
- An advanced growth process enabling local chemical control is developed (Figure 1).
- A confirmed new record efficiency of 12.5% is demonstrated on a CZTSe device (previous record is 11.6% by IBM[1]) (Figure 2).
- The local chemical composition and oxidation have been significantly modified during the growth process (Figure 3).
- The long-standing challenge of band gap or potential fluctuation in the field of kesterite solar cell has been greatly suppressed (Figure 4).

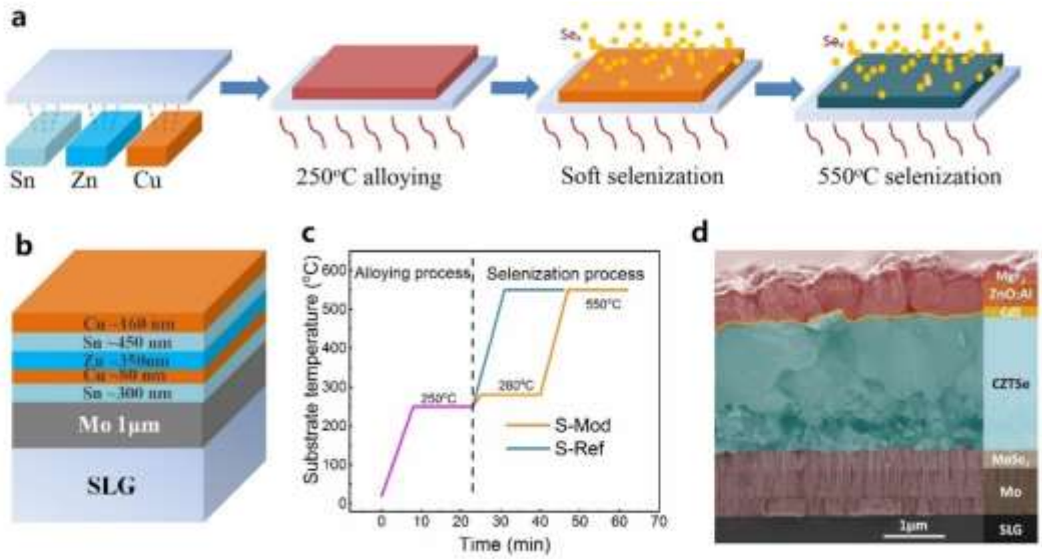

Fig. 1. Fabrication of CZTSe films and devices. | a Schematics of sputtering, annealing, and two-step selenization processes. **b** Stacking structure of metal precursors. **c** Temperature profiles of the fabrication of reference sample S-Ref and sample S-Mod with modified growth process. **d** Cross-section image of a finished CZTSe device.

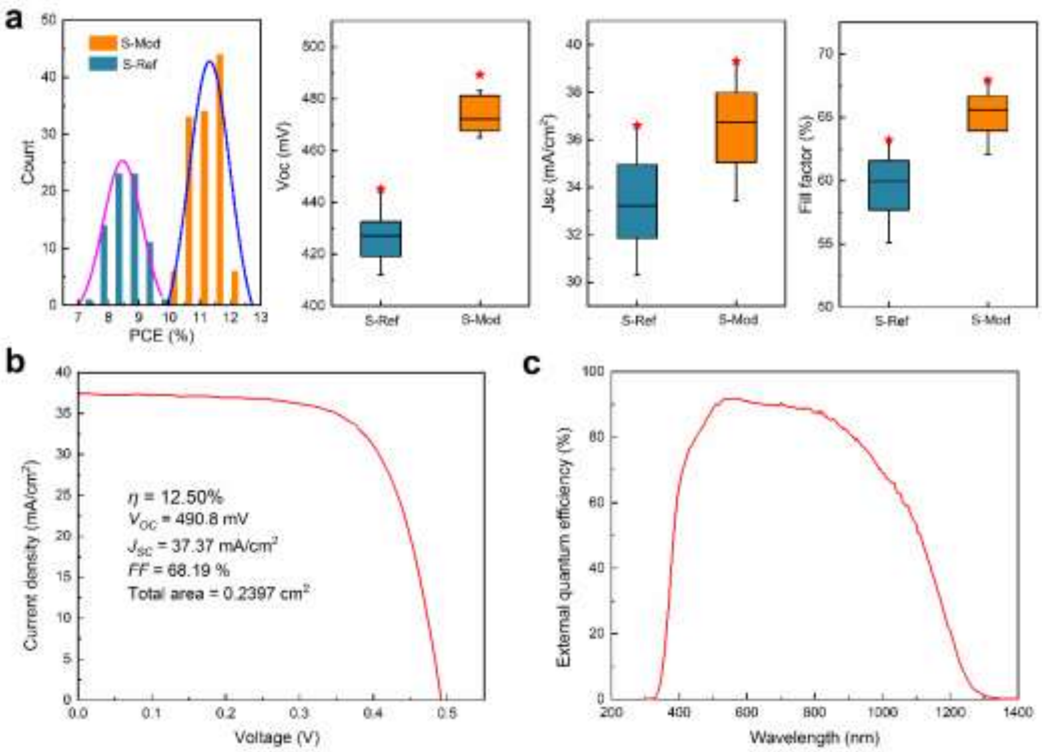

Fig. 2. Photovoltaic performance. | **a** Statistical box and histogram plots of device performance parameters of S-Mod and S-Ref. The sample size is 124 cells for S-Mod and 73 cells for S-Ref. All the photovoltaic performance parameters are measured based on total area devices. **b** Certified J-V data and **c**, EQE data of the champion CZTSe solar cell from S-Mod.

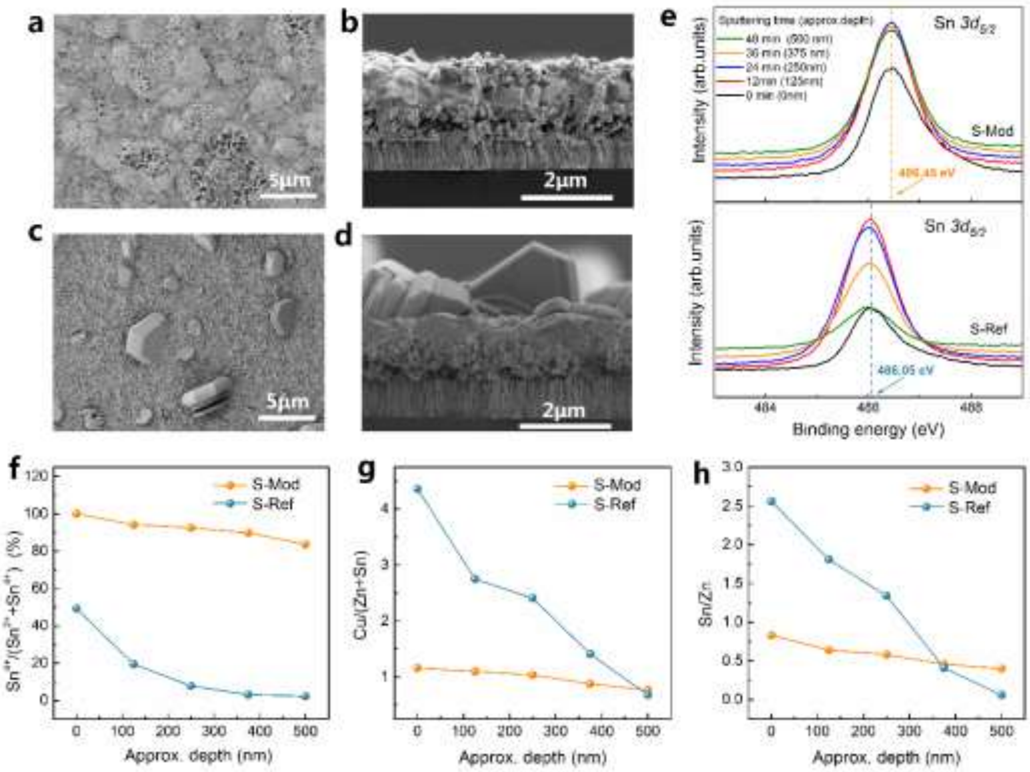

Fig. 3. Morphologies, oxidation states of Sn, and local chemical compositions of half-selenized samples. | Surface and cross-section SEM images of **a, b** half-selenized S-Mod and **c, d** half-selenized S-Ref. **e** Sn 3d5/2 XPS depth profiles of half-selenized S-Mod and half-selenized S-Ref. **f** Depth profile of proportion of Sn4+ in Sn ions, **g** ratio of Cu/(Zn+Sn), and **h** ratio of Sn/Zn for half-selenized S-Mod and half-selenized S-Ref.

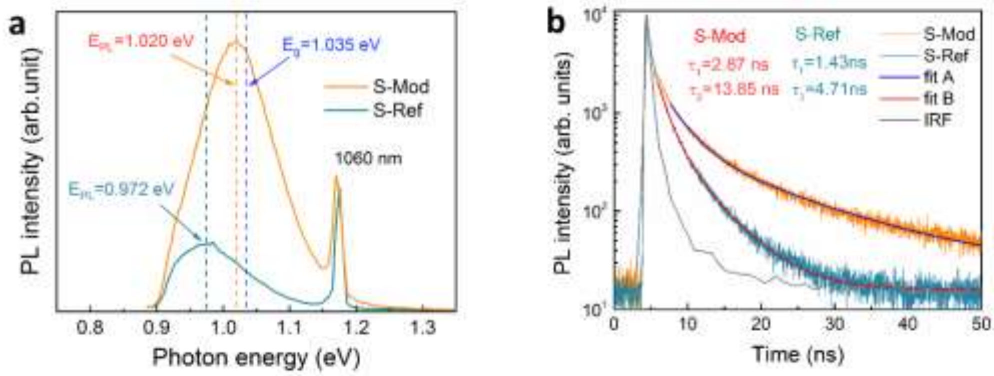

Fig. 4. Carrier recombination mechanisms and defect profiles. | a, b PL and TRPL spectra for S-Mod and S-Ref. The PL peaks at 1060 nm in **a** is the binary divided frequency signals of the 530 nm laser.

References

Lee, Y. S., Gershon, T., Gunawan, O., Todorov, T. K., Gokmen, T., Virgus, Y., & Guha, S., 2015. 'Cu2ZnSnSe4 thin-film solar cells by thermal co‐evaporation with 11.6% efficiency and improved minority carrier diffusion length', *Advanced Energy Materials*, 5(7), 1401372.