

## Supporting Information

### **Efficiency Improvement of Sb<sub>2</sub>Se<sub>3</sub> Solar Cell via Grain Boundary Inversion**

Chao Chen,<sup>#,†,§</sup> Kanghua Li,<sup>#,†,§</sup> Shiyu Chen,<sup>‡</sup> Liang Wang,<sup>#,†</sup> Shuaicheng Lu,<sup>#,†</sup>

Yuhao Liu,<sup>#,†</sup> Dengbing Li,<sup>#,†</sup> Haisheng Song,<sup>#,†</sup> and Jiang Tang<sup>\*,#,†</sup>

<sup>#</sup>Wuhan National Laboratory for Optoelectronics (WNLO), Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan, 430074, Hubei, P. R. China.

<sup>†</sup>Shenzhen R&D Center of Huazhong University of Science and Technology, Shenzhen, 518000, P. R. China.

<sup>‡</sup>Key Laboratory of Polar Materials and Devices (MOE), East China Normal University, Shanghai 200241, China

## **EXPERIMENTAL METHODS**

### **Solar cell fabrication**

All devices were deposited on glass-coated ITO supplied by Kaivo (Zhuhai, China) that had been pre-cleaned using a detergent, acetone, isopropanol and water rinse in sequence with each step for 30 min. A 60 nm thick CdS layer was deposited by chemical bath deposition at 65 °C for 16 min.<sup>1</sup> Then the CdS buffer layer was treated by CdCl<sub>2</sub> anhydrous methanol solution (0.2 M) through spin-coating process, subsequently annealed at 400 °C for 5 min in air atmosphere.<sup>1</sup> The Sb<sub>2</sub>Se<sub>3</sub> layer was deposited on ITO/CdS substrate by rapid thermal evaporation (RTE) procedure in a tube furnace (MTI, Hefei, China) with Sb<sub>2</sub>Se<sub>3</sub> powder (99.999% purity, Jiangxi Ketai Advanced Materials, Co., Ltd.) under a vacuum pressure of ~1 pa. The details can be found in our previous paper.<sup>2</sup> Au electrodes were deposited by the electron beam and resistance evaporation thin film deposition system (Beijing Technol Science, Co., Ltd.) under a vacuum pressure of 5×10<sup>-3</sup> Pa. The area of each device is 0.09 cm<sup>2</sup>. Then the same sample was cut into two parts. One part without treatment served as the control device; and the other one was treated by CuCl<sub>2</sub> and/or (NH<sub>4</sub>)<sub>2</sub>S.

### **CuCl<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>S treatment**

CuCl<sub>2</sub> solution was prepared by dissolving 13.4 mg (or 67.0 mg) CuCl<sub>2</sub> powder into 10 mL ammonia aqueous solution (28% wt.) with the Cu ion concentration of 0.01 (or 0.05) mol L<sup>-1</sup>. The CuCl<sub>2</sub> powder dissolved in ammonia aqueous very quickly (less than 30 seconds). The obtained precursor color is blue for 0.01 mol

L<sup>-1</sup> solution and dark blue for 0.05 mol L<sup>-1</sup> solution. The devices without Au electrodes (ITO/CdS/Sb<sub>2</sub>Se<sub>3</sub>) were soaked in the solution for 10 min at room temperature in ambient air, subsequently washed by deionized water for twice and dried by N<sub>2</sub> gas. For (NH<sub>4</sub>)<sub>2</sub>S treatment, the device was put on spin coater, then 3 mL (NH<sub>4</sub>)<sub>2</sub>S solution (0.3 mmol L<sup>-1</sup>) was dropped onto the Sb<sub>2</sub>Se<sub>3</sub> film rotating at a speed of 2500 rpm. Subsequently, the rotating Sb<sub>2</sub>Se<sub>3</sub> film was rinsed by 3mL deionized water for 1 min. Finally, the device was dried by N<sub>2</sub> gas.

### **Solar-cell performance measurement**

The current density–voltage (J–V) curves were measured under simulated AM1.5G (100 mW cm<sup>-2</sup>) illumination from a 450 W xenon light source (Oriel, Model 9119, Newport) with a source meter (Keithley 2400) in air at room temperature. Before the measurement, the light source was kept on for 30 min, then the light intensity was calibrated with a standard Si solar cell (Oriel, Model 91150V, Newport).

### **Cu ion diffusion coefficient measurement**

Sb<sub>2</sub>Se<sub>3</sub> thin films of approximately 400 nm was deposited on ITO by standard RTE process, which were treated by 0.01 mol L<sup>-1</sup> CuCl<sub>2</sub> ammonia aqueous solution for 10 minutes, and then cleaned by deionized water (DI-water) for twice and dried with dry N<sub>2</sub> gas before depositing Au electrode. Dependence of resistivity on duration of annealing ( $\rho$ - $t$  curves) was used for estimation of effective diffusion coefficient ( $D$ ) of Cu in Sb<sub>2</sub>Se<sub>3</sub>. The devices were annealed at fixed temperature (50°C, 80°C, 100°C, 120°C, 130°C and 150°C) for different

time (5 min, 10 min, 15 min, 20 min, 25 min and 30 min). I-V measurements were carried out at each temperature for each time using Agilent B1500A.

### **Material characterization**

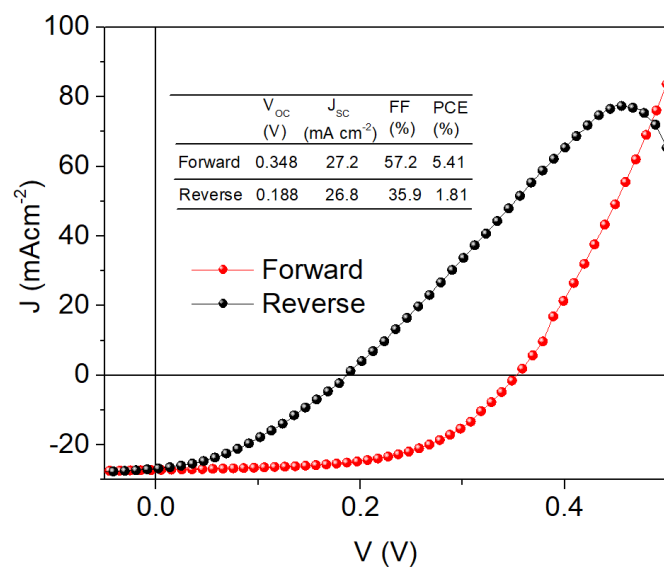
SIMS was performed by a time-of-flight secondary ion mass spectrometry (TOF-SIMS 5, ION-TOF) in the positive ion mode. 10 keV Ar gas cluster ion beam (GCIB) was used to sputter. The sputtering rate was about  $2 \text{ nm s}^{-1}$ . The vacuum of the chamber was about  $8 \times 10^{-10}$  torr. The charge was neutralized by a low energy electron gun. KFPM (Bruker Dimension EDGE) measurements were performed on our samples in a grounded manner using a veeco multimode V system. Topography and the local contact potential difference (LCPD) were simultaneously measured using a MESP probe (Bruker, Co/Cr coated) and sampling at a rate of 0.25 Hz. For EBIC measurements, the device of ITO/CdS/Sb<sub>2</sub>Se<sub>3</sub>/Au was placed into an SEM vacuum chamber. A Quanta 400 FEG FEI microscope equipped with a Smart EBIC (Gatan, Inc.) were used to enable SEM images. The gold back contact and ITO front contact were collected to the preamplifier by a small micromanipulator to obtain voltage-current signals. The electron-beam voltage and working distance was 20 kV and 10.5 mm, respectively.

### **Calculations Methods**

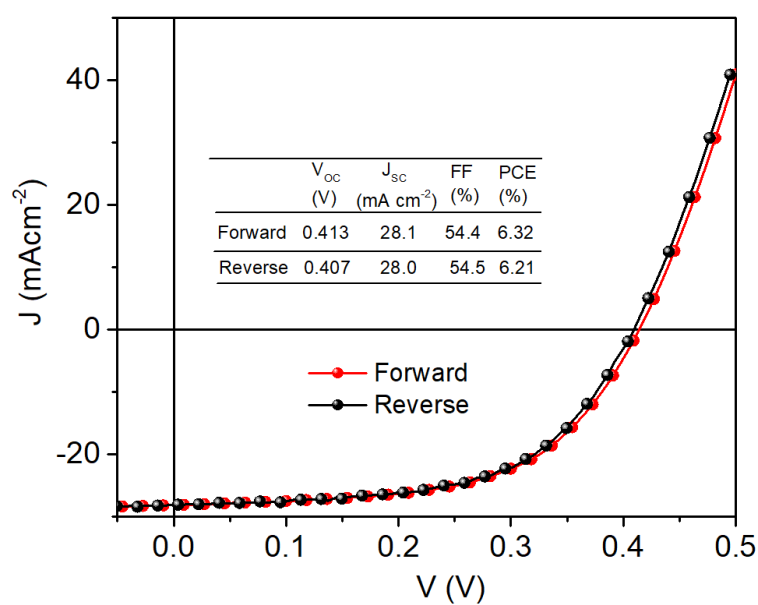
First principles calculations based on the density functional theory formalism were performed using the Vienna Ab Initio Simulation Package code.<sup>3</sup> The semilocal generalized gradient approximation functional (in the Perdew–Burke–

Ernzerhof form) was used for the exchange-correlation functional and the projector augmented wave pseudopotentials were employed for treating the influence of the core electrons, with an energy cutoff 400 eV for the plane wave basis. The defect properties were calculated using the  $3 \times 1 \times 1$  supercell model.

- (1) Ambient  $\text{CdCl}_2$  Treatment on CdS Buffer Layer for Improved Performance of  $\text{Sb}_2\text{Se}_3$  Thin Film Photovoltaics. *Appl. Phys. Lett.* **2015**, *107*, 143902.
- (2) Zhou, Y.; Wang, L.; Chen, S.; Qin, S.; Liu, X.; Chen, J.; Xue, D.; Luo, M.; Cao, Y.; Cheng, Y.; et al. Thin-Film  $\text{Sb}_2\text{Se}_3$  Photovoltaics with Oriented One-Dimensional Ribbons and Benign Grain Boundaries. *Nat. Photonics* **2015**, *9*, 409-415.
- (3) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47*, 558.



**Figure S1.** The forward (from  $V_{OC}$  to  $J_{SC}$ ) and backward (from  $J_{SC}$  to  $V_{OC}$ ) current density-voltage scans of  $Ag^+$  treated  $Sb_2Se_3$  device. Distinct hysteresis is observed. The treatment process is the same as  $CuCl_2$  treatment, but the precursor is 0.01 mol L<sup>-1</sup> aqueous  $AgNO_3$  solution instead.



**Figure S2.** The forward (from  $V_{OC}$  to  $J_{SC}$ ) and backward (from  $J_{SC}$  to  $V_{OC}$ ) current density-voltage scans of  $CuCl_2$  treated  $Sb_2Se_3$  device. Nearly no hysteresis is

observed.

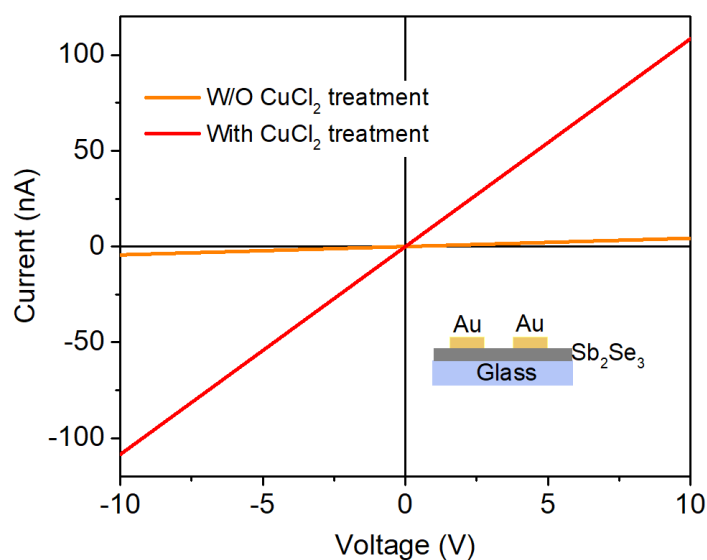


Figure S3. The dark current of  $\text{Sb}_2\text{Se}_3$  with and without  $\text{CuCl}_2$  treatment.

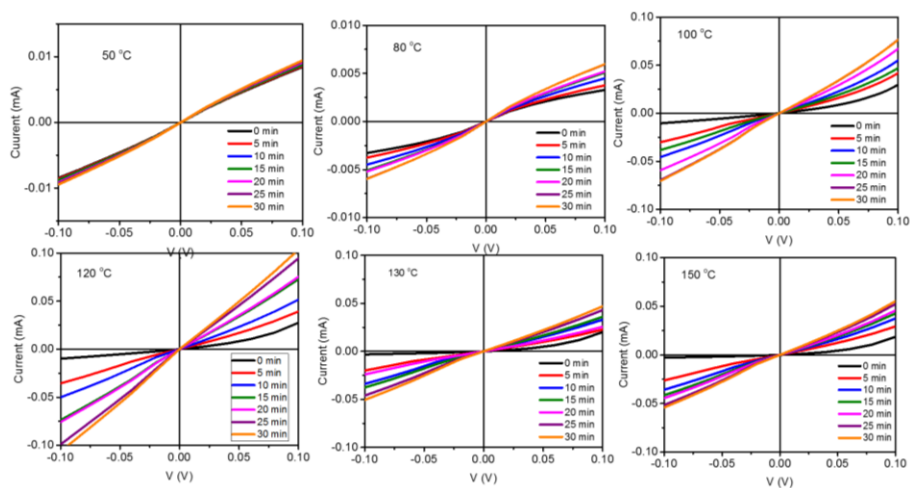
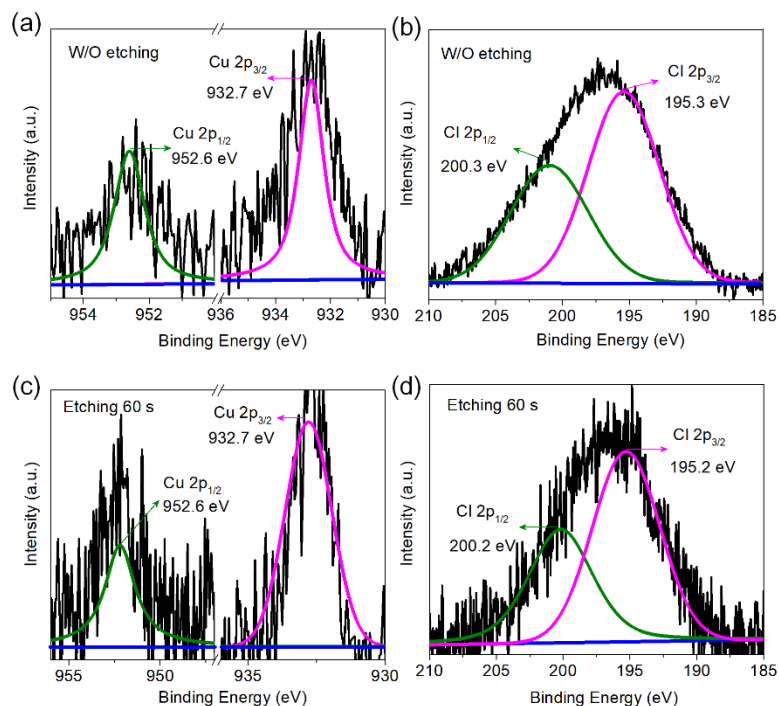
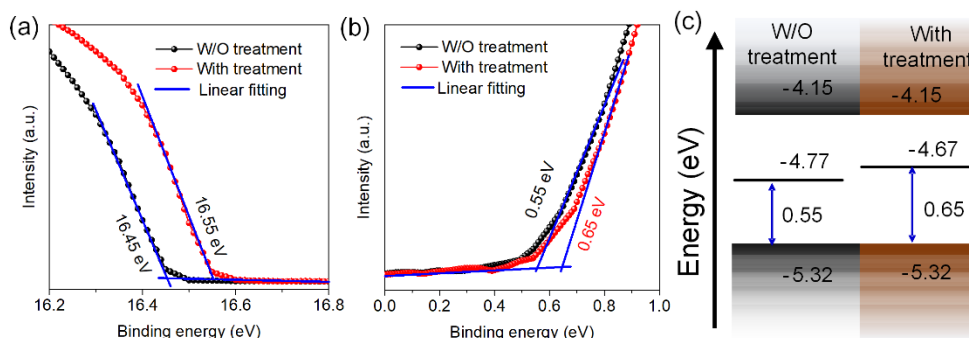


Figure S4. The time dependent current-voltage curves of ITO/ $\text{Sb}_2\text{Se}_3$ /Au at different annealing temperature. The  $\text{Sb}_2\text{Se}_3$  films were treated by  $\text{CuCl}_2$ .



**Figure S5. X-ray photoelectron spectroscopy (XPS) characterization of untreated and CuCl<sub>2</sub> treated Sb<sub>2</sub>Se<sub>3</sub> films.** XPS spectra of (a) Cu 2p and (b) Cl 2p of Sb<sub>2</sub>Se<sub>3</sub> film surface without etching. XPS spectra of (c) Cu 2p and (d) Cl 2p of Sb<sub>2</sub>Se<sub>3</sub> film surface with etching for 60 s. The intensity of Cu 2p were very noisy, indicating the low content of Cu and Cl. Through the peak position of Cu 2p XPS, we confirm the valence of Cu is +2.



**Figure S6. Ultraviolet photoelectron spectroscopy (UPS) measurements of Sb<sub>2</sub>Se<sub>3</sub> film with and without CuCl<sub>2</sub> treatment (a, b) and the corresponding band position**



**(c). Clearly, the conduction band and valence band of the  $\text{CuCl}_2$  treated sample were unchanged, but the Fermi level moved closer to conduction band.**