Supporting Information

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Characterization of basic physical properties of Sb_2Se_3 and its relevance for photovoltaics

Chao CHEN[1], David C. BOBELA[2], Ye YANG[2], Shuaicheng LU[1], Kai ZENG[1], Cong GE[1], Bo YANG[1], Liang GAO[1], Yang ZHAO[1], Matthew C. BEARD[2], Jiang TANG (✉)[1]

1 Wuhan National Laboratory for Optoelectronics (WNLO), Huazhong University of Science and Technology, Wuhan 430074, China
2 Chemistry and Nanoscience Center, National Renewable Energy Laboratory, Golden, CO, 80401, USA
Corresponding author: jtang@mail.hust.edu.cn

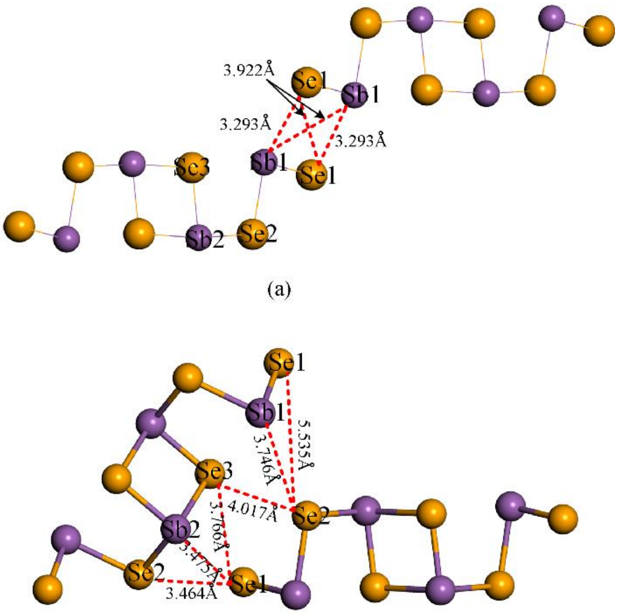
1. Biased internal quantum efficiency (IQE) measurement

Before IQE measurement, we carried out transmissivity and reflectivity spectrum using Lambda 950 (Perkin Elmer). For external quantum efficiency (EQE) measurement, light source was generated by a 300 W xenon lamp of Newport (Oriel, 69911) and then split into monochromatic light using Newport oriel cornerstone™ 130 1/8 Monochromator (Oriel, model 74004). A reference standard silicon solar cell was used for calibration. A Keithley 2400 source meter was used to apply bias.

2. Photothermal deflection spectroscopy (PDS) measurement

The PDS measurements were made in transverse mode [1], using reflective optics to guide the pump beam from a single grating monochromator to a sample. The pump beam was chopped at 6 Hz and was focused to a spot size of approximately 1 mm. The samples were kept in a helium purged glove box, until time of measurement, when they were loaded into a quartz cuvette and immersed in anhydrous perfluorohexane. The probe beam consisted of ~2 mW, 633 nm laser light from an intensity stabilized helium-neon laser. Alignment of the probe beam was made using a 3 axis stage and care was taken to avoid sample illumination from the probe beam. Probe beam deflections measured by a silicon photo-diode were amplified and processed using lock-in methods.

3. Inter-atom distance in Sb_2Se_3



(a)

(b)

Fig. S1 Measured inter-atom distances of Sb-Sb, Sb-Se and Se-Se in Sb_2Se_3 crystal

4. Capacitance-voltage (*C*-*V*) measurement

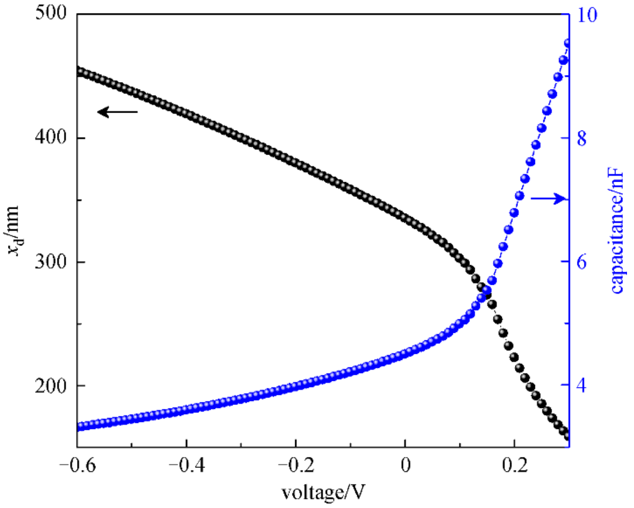


Fig. S2 *C*-*V* characteristics of the devices were tested at room temperature in darkness at a frequency of 10 kHz and AC amplitude of 30 mV. DC bias voltage was swept from −0.6 to 0.3 V. According to the formulation, $x_d(V)=\varepsilon A/C(V)$ [where $x_d(V)$ and $C(V)$ are the voltage dependence of depletion width and capacitance, respectively, ε is the dielectric constant of Sb_2Se_3 at 10 kHz, and A is the electrode area], the voltage dependence of depletion width was shown as black dots

5. Bias dependent IQE spectra

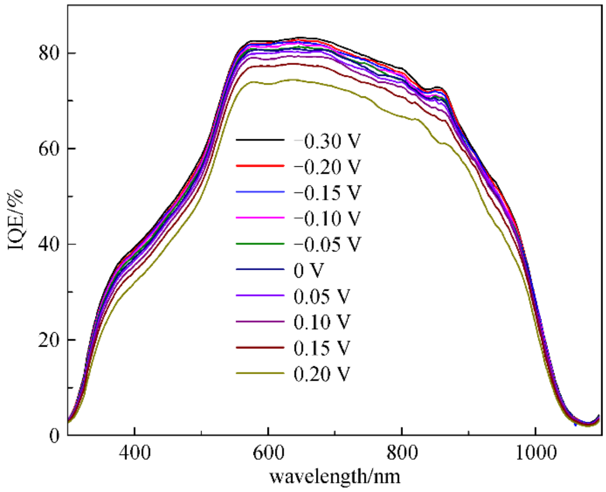


Fig. S3 IQE spectra of Sb_2Se_3 solar cells measured under various biases. The IQE was calculated as EQE/(1−*R*−*T*)

6. Derivation of the anisotropic mobility

As shown in Fig. S4, the unit vector of $\overrightarrow{\mathbf{OP}}$ is

$$\overrightarrow{\boldsymbol{e}_{\mathrm{OP}}}=\left(\frac{h}{\sqrt{h^2+k^2+l^2}},\frac{k}{\sqrt{h^2+k^2+l^2}},\frac{l}{\sqrt{h^2+k^2+l^2}}\right). \qquad \text{(S1)}$$

Ignoring the nonlinear effect, the mobility matrix is diagonal as

$$\boldsymbol{M}=\begin{pmatrix}\mu_a & 0 & 0\\ 0 & \mu_b & 0\\ 0 & 0 & \mu_c\end{pmatrix}, \qquad \text{(S2)}$$

where μ_a, μ_b and μ_c are the mobilies along the *a*-, *b*- and *c*-direction.

The mobility along $\overrightarrow{\mathbf{OP}}$ direction is

$$\begin{aligned}\overrightarrow{\mu_{[hkl]}}&=\overrightarrow{\boldsymbol{e}_{\mathrm{OP}}}\boldsymbol{M}\\ &=\left(\frac{h}{\sqrt{h^2+k^2+l^2}},\frac{k}{\sqrt{h^2+k^2+l^2}},\frac{l}{\sqrt{h^2+k^2+l^2}}\right)\begin{pmatrix}\mu_a & 0 & 0\\ 0 & \mu_b & 0\\ 0 & 0 & \mu_c\end{pmatrix} \qquad \text{(S3)}\\ &=\left(\frac{h\mu_a}{\sqrt{h^2+k^2+l^2}},\frac{k\mu_b}{\sqrt{h^2+k^2+l^2}},\frac{l\mu_c}{\sqrt{h^2+k^2+l^2}}\right).\end{aligned}$$

So $\mu_{[hkl]}$ is

$$\mu_{[hkl]}^2=\frac{h^2}{h^2+k^2+l^2}\mu_a^2+\frac{k^2}{h^2+k^2+l^2}\mu_b^2+\frac{l^2}{h^2+k^2+l^2}\mu_c^2. \qquad \text{(S4)}$$

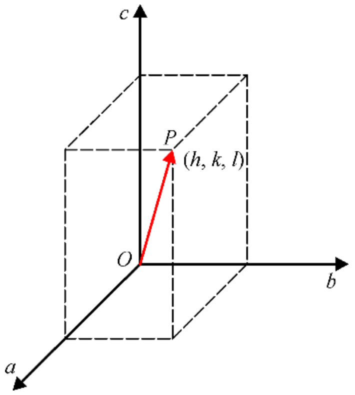


Fig. S4 Decomposition of anisotropic mobility in Sb_2Se_3. ***A***, ***b*** and ***c*** is the lattice vector corresponding to [100], [010] and [001] axis. $\overrightarrow{\mathbf{OP}}$ is the normal vector of crystal face (*hkl*)

7. Space charge limited current (SCLC)

The defect density can be extracted from SCLC measurement at the transition regime between the linear region and the quadratic region by Eq. (S5) [1]:

$$n_{\mathrm{t}} = \frac{2\varepsilon_{\mathrm{r}}\varepsilon_0 V_{\mathrm{TFL}}}{qd^2}, \tag{S5}$$

where V_{TFL}=16.5 V is the turning point between linear and non-linear regime representing the onset voltage of the trap filled limit (TFL) as shown in Fig. S5. ε_0 is the vacuum permittivity, ε_{r}=29 is the dielectric constant of Sb_2Se_3 at low frequency, q is the elementary charge, n_{t} is the trap density and d is the thickness of Sb_2Se_3. The trap density n_{t} was estimated as 6.9×10^{14} cm^{-3} based on the SCLC result.

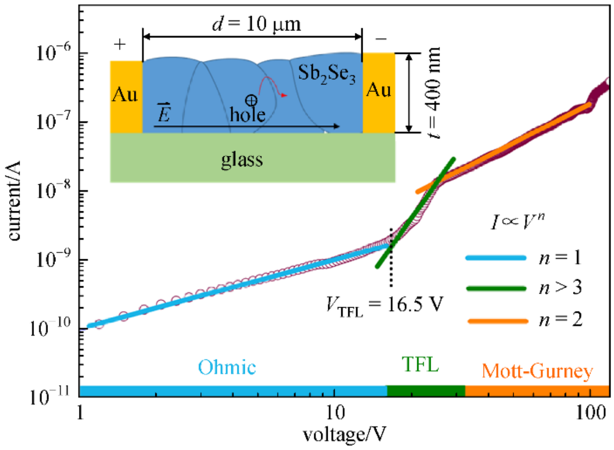


Fig. S5 Mobility measurements of Sb_2Se_3 film. The bilogarithmic *I*-*V* curves. The inset is the device configuration for SCLC measurement

8. Theory and experimental results of Hall measurement

The formula of Hall coefficient is shown as Eq. (S6) [2].

$$R_{\mathrm{H}} = \frac{1}{q}\frac{p\mu_{\mathrm{h}}^2 - n\mu_{\mathrm{e}}^2}{\left(p\mu_{\mathrm{h}} + n\mu_{\mathrm{e}}\right)^2}. \tag{S6}$$

To replace $\mu_{\mathrm{e}}/\mu_{\mathrm{h}}$ with b for simplification, the Hall coefficient is simplified to Eq. (S7).

$$R_{\mathrm{H}} = \frac{1}{q}\frac{p-nb^2}{(p+nb)^2}. \tag{S7}$$

If the intrinsic excitation is dominant at high temperature, $n_i = n = p$, the Hall coefficient can be simplified to Eq. (S8).

$$R_{\mathrm{H}} = \frac{1}{qn_{\mathrm{i}}}\frac{1-b}{1+b}. \tag{S8}$$

The relation of conductivity and mobility follows Eq. (S9).

$$\sigma = n_{\mathrm{i}}q(\mu_{\mathrm{e}} + \mu_{\mathrm{h}}). \tag{S9}$$

The Hall mobility can be written as Eq. (S10).

$$\mu = |R_{\mathrm{H}}\sigma| = |\mu_{\mathrm{h}} - \mu_{\mathrm{e}}|. \tag{S10}$$

In addition, the carrier concentration is written as Eq. (S11).

$$n = p = \frac{1}{qR_{\mathrm{H}}} = n_{\mathrm{i}}\frac{1+b}{1-b}. \tag{S11}$$

Under the intrinsic excitation, if the electron mobility is larger than that of hole, the Hall coefficient will be negative.

Hall effect measurement was conducted on Ecopia HMS-5500 using the device structure Sb_2Se_3/glass with the size of 3 mm×3 mm× 400 nm in dark. All four electrodes are Au. The applied magnetic field intensity was 0.56 T. The temperature was controlled by resistive heating. Before test, we waited for 15 min to ensure temperature stabilization (Fig. S6).

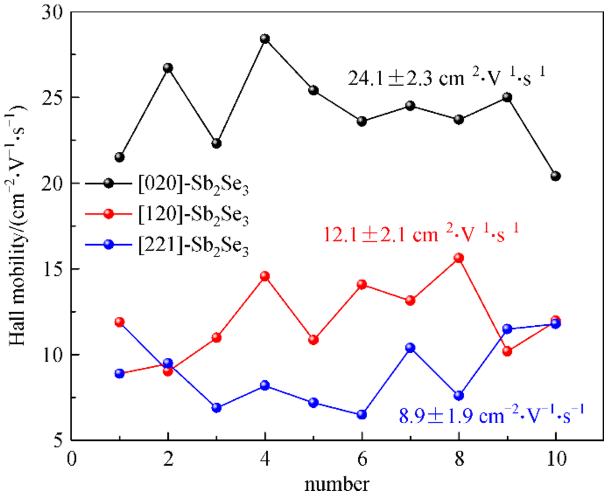


Fig. S6 Hall mobility $|\mu_e - \mu_h|$ of 24.1±2.3, 12.1±2.1 and 8.9±1.9 cm^2·V^{-1}·s^{-1} were measured at 380 K for [020]-, [120]- and [221]-Sb_2Se_3 films

Reference:

1. Jackson W B, Amer N M, Boccara A, Fournier D. Photothermal deflection spectroscopy and detection. Applied Optics, 1981, 20(8): 1333