## **Supporting Information**

## Realizing high thermoelectric performance in highly (0/0)-textured flexible Cu<sub>2</sub>Se thin film for wearable energy harvesting

Zhuang-Hao Zheng<sup>a</sup>, Dong-Liang Zhang<sup>a</sup>, Bushra Jabar<sup>a</sup>, Tian-Bao Chen<sup>a</sup>, Mohammad Nisar<sup>a</sup>, Yun-Fei Chen<sup>c</sup>, Fu Li<sup>a</sup>, Shuo Chen<sup>a</sup>, Guang-Xing Liang<sup>a</sup>, Xiang-Hua Zhang<sup>b</sup>, Ping Fan<sup>a</sup>, Yue-Xing Chen<sup>a</sup>\*

a Shenzhen Key Laboratory of Advanced Thin Films and Applications, Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, P. R. China b Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) UMR6226, Rennes, F-35000, France

c Hangzhou Innovation Institute, Beihang University, Hangzhou, 310052, P. R. China

Operating duration (min)	0	3	5	7	9	11
Thickness(nm)	380	410	430	450	455	465
Cu (at.%)	66.6	67.3	68.5	68.8	69.4	69.8
Se (at.%)	33.4	32.7	31.5	31.2	30.6	30.2
Cu:Se	1.99	2.05	2.17	2.20	2.26	2.31

Table S1 Composition and thickness of  $Cu_2Se$  based thermoelectric film and corresponding operating time of Cu target.



Fig.S1. (010) orientation strength of films in different proportions

To determine the effect of the preferred orientation on the growth conditions, Fig.S1 shows the calculated Lotgering factor (F) of the (0l0) planes for all films. This factor is calculated as[1, 2]

$$F = \frac{P - P_0}{1 - P_0} \tag{1}$$

$$P = \frac{I_0(00l)}{\sum I(h \ k)l} \tag{2}$$

$$P_{0} = \frac{I_{0}(00l)}{\sum I_{0}(h \ k)l}$$
(3)

where I(0l0) is the total diffraction intensity of the (0l0) plane,  $\sum I$  (hkl) is the total intensity of all (*hkl*) diffraction peaks, and *P* is the ratio of intensity of the (0l0) plane at the measurement date.  $I_0(0l0)$ ,  $I_0(hkl)$ , and  $P_0$  represent the corresponding parameters for the standard patterns (PDF#37-1187).



Fig.S2. XRD refinement of Cu-9mins (a) and Cu-11mins (b) films.



Fig.S3. Three-dimensional XRD poles at different positions:(a) (030), (b) (060) of Cu-7mins sample.



Fig.S4. Surface morphologies of the film with different Cu:Se atomic ratios of 2.17:1 (a), 2.31:1 (b).



**Fig.S5.** Strain mapping corresponding to HRTEM images Cu-7mins thin film (color online). Here GPA strain maps with (b) strain along x-axis and (c) strain along y-axis are correspondingly related to (a), and GPA strain maps (e) strain along x-axis and (f) strain along y-axis are related to (d); the color scale shows the induced strain ranges from -0.48 % to 2.43%



**Fig.S6.** (a) The effective mass changes with Cu content. (b) Seebeck coefficient versus hole concentration (n) at room temperature. The lines are calculated by single-band model.

We perform a data simulation in an easy-to-understand manner and in a single parabola manner,

which allows us to fully understand the observed transport properties, as illustrated by the following equation:[3, 4]

$$S(\eta) = \frac{k_B}{e} \cdot \left[ \frac{\left(r + \frac{5}{2}\right) \cdot F_{r + \frac{3}{2}}(\eta)}{\left(r + \frac{3}{2}\right) \cdot F_{r + \frac{1}{2}}(\eta)} - \eta \right]$$
(4)

$$n_{H} = \frac{1}{e.R_{H}} = \frac{(2m^{*}.k_{B}T)^{\frac{3}{2}}}{3\pi^{2}\hbar^{3}} \cdot \frac{\left(r + \frac{3}{2}\right)^{2}.F_{r + \frac{1}{2}}^{2}(\eta)}{\left(2r + \frac{3}{2}\right).F_{2r + \frac{1}{2}}(\eta)}$$
(5)

$$\mu_{H} = \left[\frac{e\pi\hbar^{4}}{\sqrt{2}(k_{B}T)^{\frac{3}{2}}} \frac{C_{1}}{E_{def}^{2}(m^{*})^{\frac{5}{2}}}\right] \frac{\left(2r+\frac{3}{2}\right) \cdot F_{2r+\frac{1}{2}}(\eta)}{\left(r+\frac{3}{2}\right)^{2} \cdot F_{r+\frac{1}{2}}(\eta)}$$
(6)

where  $\eta$  and  $k_B$  are the reduced Fermi level and the Boltzmann constant. *e* and *r* are the electron charge and the carrier scattering factor ( $\mathbf{r} = -1/2$  for acoustic phonon scattering).  $R_H$  and  $m^*$  are the Hall coefficient, the effective mass.  $\hbar$  and  $C_1$  are the reduced Plank constant and the elastic constant for longitudinal vibrations and the deformation potential coefficient. Pay attention to this formula  $C_1 = v_1^2$ .  $\rho$ , where  $v_1$  is the longitudinal sound velocity. Due to the difficulty of measuring the longitudinal sound velocity of Cu<sub>2</sub>Se at present, we used the universal value (3350 m/s) as a substitute. Finally,  $F_i(\eta)$  is the Fermi integral and can be expressed as

$$F_i(\eta) = \int_0^\infty \frac{x^i}{1+e^{(x-\eta)}} dx \tag{7}$$

Based on the above formula, we can end up with several specific values including effective mass  $m^*$ and  $E_{def}$ .



**Fig.S7.** Corresponding density of states (DOS) and partial density of states (PDOS) of (a)  $\beta$ -Cu<sub>2</sub>Se, DOS and PDOS of (b)  $\alpha$ -Cu<sub>2</sub>Se.

The electronic band structure and density of states (DOS) for  $\beta$ -Cu<sub>2</sub>Se,  $\alpha$ -Cu<sub>2</sub>Se are performed by first-principles plane-wave pseudopotential formalism as implemented in the VASP package [5, 6]. The ion-electron interaction is modelled with the help of the projector-augmented wave (PAW) [7] method for Cu and Se atoms. Cutoff energy for the wave function is set to 600 eV. The generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) is adopted for the exchange and correlation functional. The structures have been relaxed until the forces on each atom are less than 0.02 eV/Å, and the criterion for energy convergence is set as  $1.0 \times 10^{-5}$  eV. A Monkhorst-Pack k-point mesh of  $8 \times 6 \times 2$  is adopted for the Brillouin zone sampling of the cell. The excess Cu locates in the interstitial site with the maximum space in the Cu<sub>2</sub>Se cell. The electronic energy band is plotted based on a 150 k-points grid. All the calculations are done without including spin-orbit coupling (SOC). Structures are visualized in the VESTA software [8].



Fig.S8. Lattice thermal conductivity of films with different stoichiometric ratios at different temperatures.

The value of  $\kappa_1$  is calculated by the following formula:

$$k_l = k - k_e \tag{8}$$

$$k_e = L \cdot T \cdot \sigma \tag{9}$$

the value of  $\kappa_e$  depends on three parameters: Lorentz constant L, temperature T, and electrical conductivity  $\sigma$ . In addition, Lorentz constant L is related to Seebeck coefficient S[9-11].



Fig.S9. TLM measurement model construction and its optical photograph.



Fig.S10. (a) The cross sections of Ag electrode bonded with Cu<sub>2</sub>Se film before heating. (b)

Composite electrode bonded with Cu<sub>2</sub>Se film before heating.



Fig.S11. Size and specific arrangement of Cu<sub>2</sub>Se-based thermoelectric devices.



**Fig.S12.** (a) Thermoelectric properties of devices at different temperature differences. (b) Stability of resistance at different bending times.

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