Supporting Information for

## Doping amount dependence of phase formation and microstructure evolution in heavily Cu-doped Bi<sub>2</sub>Te<sub>3</sub> films for thermoelectric applications

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					(at.%)
	Cu	Bi	Те	Bi/Te	Cu/Te
#1	-	43.85	56.15	0.78	-
#2	28.00	31.16	40.84	0.76	0.68
#3	43.67	23.76	43.67	0.54	1.00
#4	47.94	21.63	30.43	0.71	1.57

**Table S1** EDS analyses of as-deposited Cu-BT films. Cu-0.0, Cu-28.0, Cu-43.7, and Cu-47.9 weredesigned by #1, #2, #3, and #4, respectively.



Fig. S1 XRD spectra of Cu-BT films with different annealing temperatures: (a) 150 °C and (b) 300 °C.



**Fig. S2** Results of TEM analyses of Cu-43.7 annealed at 300 °C: (a) High-resolution TEM (HRTEM) images and selected area electron diffraction (SAED) pattern and (b) d-spacing analysis and HRTEM image (inset).

	Cu-0.0	Cu-28.0	Cu-43.7	Cu-47.9
Measured values	d = 3.21513 nm (015) d = 5.04808 nm (006)	d = 3.21915 nm (015) d = 5.04806 nm (006)	d = 3.22580 nm (015) d = 1.81725 nm (205)	d = 3.22384 nm (015) d = 1.81408 nm (205)
Reference (JCPDS 15-0863)	d = 3.2220 nm (015) d = 5.0780 nm (006)	d = 3.2220 nm (015) d = 5.0780 nm (006)	d = 3.2220 nm (015) d = 1.8120 nm (205)	d = 3.2220 nm (015) d = 1.8120 nm (205)

**Table S2** Values used for calculation of lattice parameters from the results of XRD analyses. Allpeaks were indexed by Bi2Te3 phase.

The calculation was performed by this equation:

 $\frac{1}{d^2} = \frac{4h^2 + hk + l^2}{3a^2} + \frac{l^2}{c^2}$ 



Fig. S3 HRTEM image of Cu-47.9 annealed at 300 °C.



Fig. S4 (a) FESEM image and EDS spectrum and (c) 3D AFM image of Cu-47.9 annealed at 500 °C.



Fig. S5 XPS spectrum of Bi element in Cu-47.9 annealed at 300 °C. The etching time was 3 min.



Fig. S6 Thickness change of Cu-BT films with/without thermal annealing.