Supporting Information

Control of phonon transport by formation of Al_2O_3 interlayer in Al_2O_3-ZnO superlattice thin films and their in-plane thermoelectric energy generating performance

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LIST

1. In-plane thermal conductivity measurement setup and theory behind the 3-ω method

The source meter (Keithley 6221, USA) was connected to both metallic pads of the setup for AC current (I_0) as shown in Fig. 1. A current, I_0, with an angular modulation frequency of 1-ω was applied to generate Joule heating and temperature fluctuations at a frequency of 2-ω. The resistance of the narrow metallic strip is proportional to the temperature that leads to a voltage fluctuation of 3-ω across the sample. A lock-in amplifier (A-B mode, SR-850, Stanford Research System, USA) connected to the two metallic pads in the middle measured the 3-ω voltage fluctuation along the narrow metallic strip. In the differential 3-ω method, the total temperature oscillation, $\Delta T\,(\omega)$, for a multilayer sample is defined as:[1]

$$\Delta \mathrm{T}(\omega) = \frac{P}{\pi \kappa_s}\left\{\frac{1}{2}\ln\left(\frac{D_s}{b^2}\right) + 0.923 - \frac{1}{2}\ln(2\omega) - \frac{i\omega}{4}\right\} + \frac{Pd_f}{2b\kappa_f} \tag{1}$$

where P is the supplied power-per-unit-length of the narrow metallic line; D_s is the thermal diffusivity; d_f is the thin film thickness; b is the width; and κ_s and κ_f are the thermal conductivities of the Si substrate and 100-nm-thick AO/ZnO superlattice thin film, respectively. $\Delta T\,(\omega)$ is obtained from measurements of the third-harmonic root-mean-square voltage drop, $V_{rms\text{-}3\omega}$, across the metallic line, using the following equation:

$$\Delta T(\omega) = \frac{2V_{rms-3\omega}}{\alpha I_0 R_0},\ \alpha = \frac{1}{R_0}\left(\frac{dR_0}{dT}\right) \tag{2}$$

where α is the temperature coefficient of the resistance, R_0, of the metallic strip (Ti/Au). Finally, κ_f is determined from Eq. (3), which can be derived from the second term in Eq. (1), as follows:

$$\kappa_f = \frac{Pd_f}{2b\{\Delta T_{s+f}(\omega) - \Delta T_s(\omega)\}} \tag{3}$$

where $\Delta T_{s+f}(\omega)$ is the temperature oscillation of the in-phase component for a SiO_2/Si substrate with a thin film and $\Delta T_s(\omega)$ is the temperature oscillation of the in-phase component without the thin film.

Thus, the in-plane thermal conductivity of thin films can, in general, be evaluated from Equation (3), provided $\Delta T_{s+f}(\omega)$ and $\Delta T_s(\omega)$ are measured separately using the 3-ω method in the 30–300 K temperature range. Fig. S1 shows the temperature oscillation of the in-phase component, $\Delta T_{s+f}(\omega)$, for the AO/ZnO superlattice thin films with AO thicknesses of 0.13 nm and 0.82 nm along with that of the bare Si substrate. Further details of the 3-ω measurements can be found in a previous report [2], [3]. The difference between the in-plane and the cross-plane thermal conductivity measurements of the films is the width of the heater. As shown in Fig. 1b, in-plane thermal conductivity of the films was measured by 3-ω method with narrow heater (i.e., 400-nm-width) and thick thermal insulating layer (~1 µm-thick SiO_2 layer) to minimize the uncertainty of the thermal conductivity in the in-plane direction as a substrate [4-7].

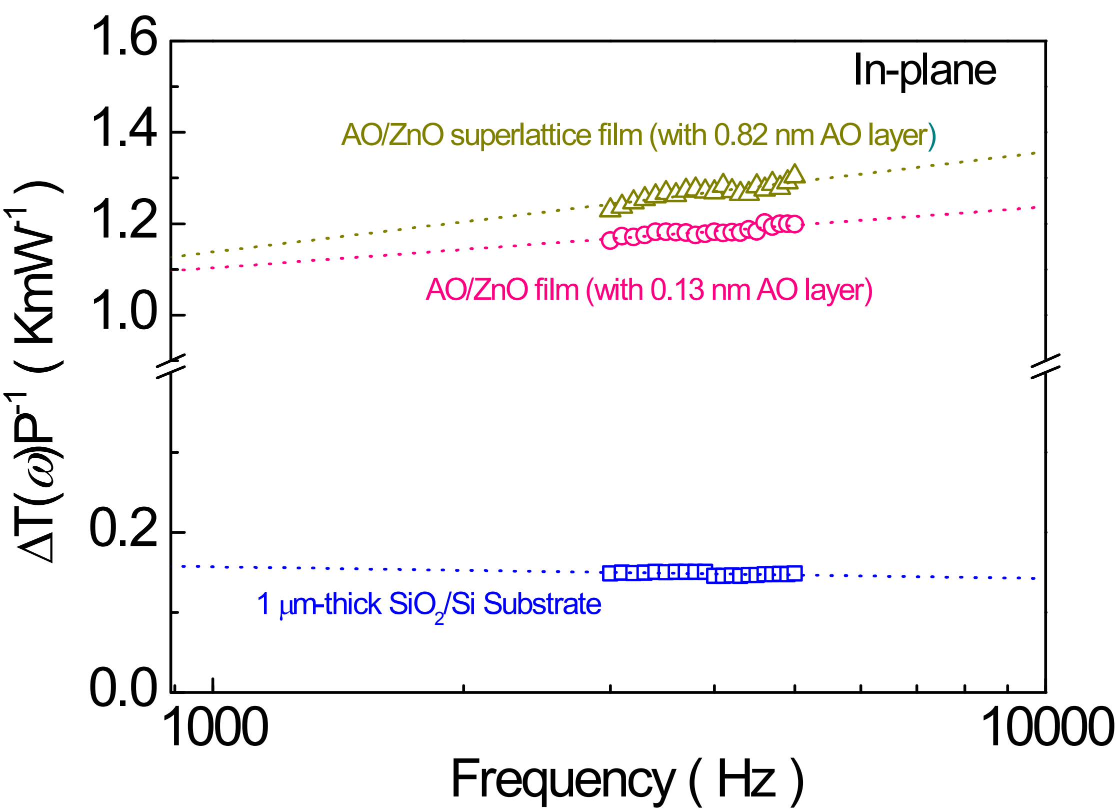

Fig. S1 Temperature oscillation of the in-phase component, $\Delta T_{s+f}(\omega)$, for the 0.13- and 0.82-nm-thick Al_2O_3 layers in Al_2O_3/ZnO superlattice thin film, where the $\Delta T_s(\omega)$ value of the 1 µm-thick-SiO_2/Si substrate is also included for reference.

2. Sample preparation and thermoelectric properties of $Bi_{0.5}Sb_{1.5}Te_3$ (BST) thin films

To fabricate the thermoelectric (TE) energy generator consisting of p-n junction legs, a $Bi_{0.5}Sb_{1.5}Te_3$ (BST) thin film was used as the p-type material, while an AO/ZnO superlattice thin film was used as the n-type material in the TE generator. In this study, a 100-nm-thick BST thin film was prepared on a SiO_2/Si substrate at room temperature via radio-frequency (RF) sputtering with a high purity bismuth antimony telluride (Bi-Sb-Te) target (99.99% purity). The base pressure of the chamber was maintained in the range of ~1.2×10^{-3} Pa prior to deposition of the films. The RF power and working pressure of the chamber during the deposition were 30 W and 2.6×10^{-1} Pa, respectively, using Ar. After deposition of the thin films, the samples were annealed at 200 °C, which is the optimized annealing temperature to enhance the TE properties of the films based on evaluation of the crystal parameters, including the crystal orientation, grain size, and lattice parameters, and surface morphologies of the samples, as well as the electrical and Seebeck coefficient of the samples; the treatment was performed over 5 min under Ar atmosphere. The in-plane electrical resistivity, Seebeck coefficient, and thermal power factor of the 100-nm-thick BST film after annealing at 200 °C were respectively determined to be ~7.7×10^{-3} Ωcm, ~390 $\mu V/K$, and ~2.7×10^{-3} W/K^2 at room temperature.

3. Measurement set-up for n-AO/ZnO superlattice/p-BST film-based TE energy generator

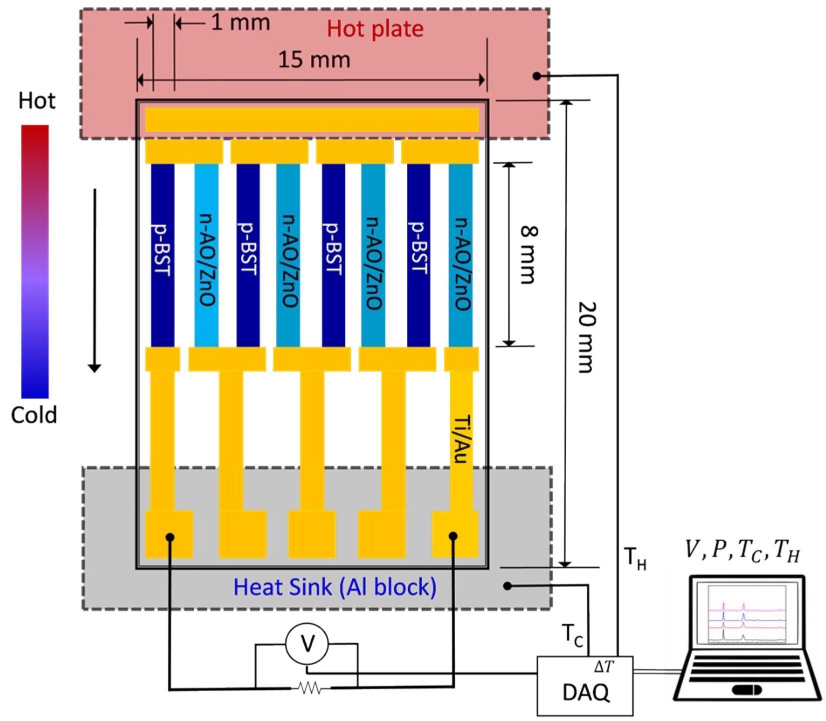

Fig. S2 Schematic images of TE energy generator, consisting of four pairs of 100-nm-thick n-AO/ZnO superlattice and p-BST thin-film legs on the substrate for the measurement of open circuit output voltage and output power of the energy generator.

4. COMSOL simulation results for n-ZnO/p-BST and n-BT/p-BST TE devices

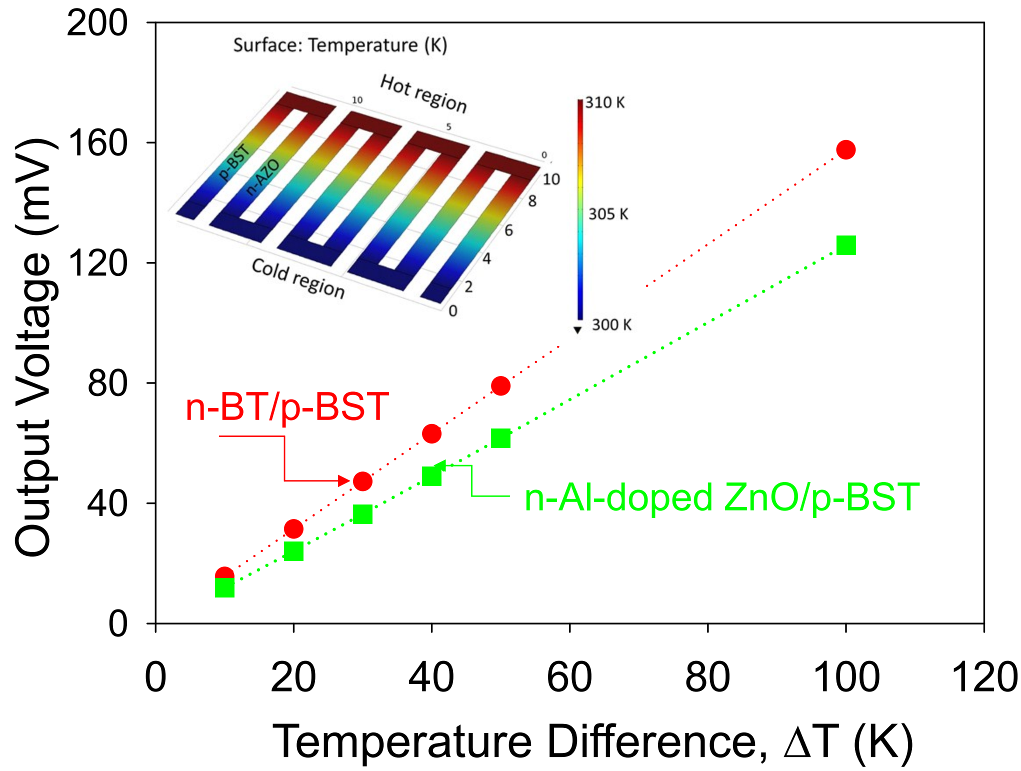

Fig. S3 Maximum output voltages of n-Al-doped ZnO/p-BST and n-bismuth telluride (BT)/p-BST thin-film-based TE energy generators as a function of temperature difference up to 100 K using COMSOL software. The inset shows temperature distribution of the n-Al-doped ZnO/p-BST TE energy generator.

5. Photocurrent effect on n-AO/ZnO films/p-BST film-based TE energy generator

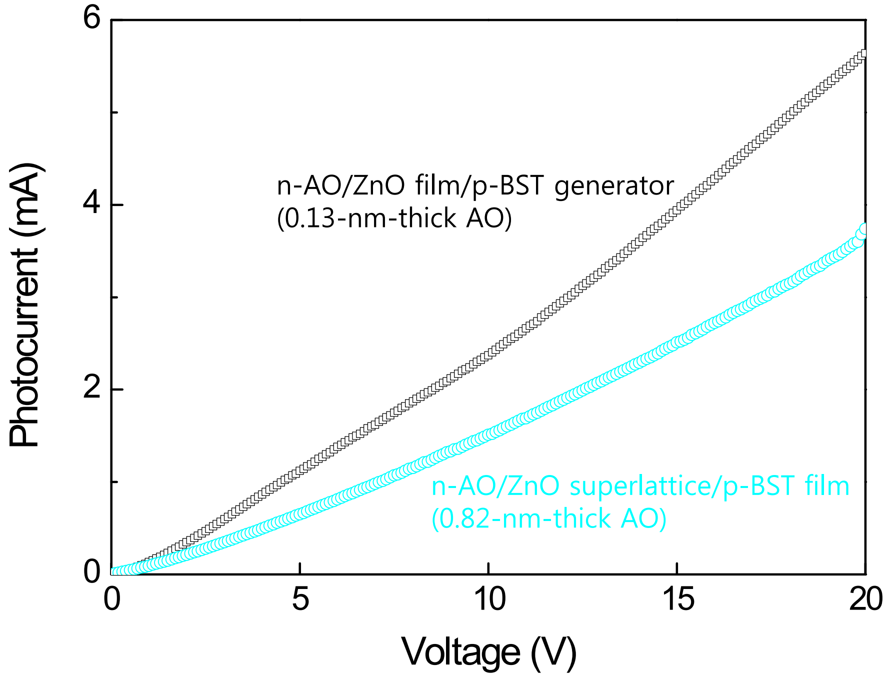

Fig. S4 Photocurrent characteristics of 100-nm-thick n-AO/ZnO superlattice (0.82-nm-thick AO)/p-BST thin-films together with n-AO/ZnO film (0.13-nm-thick AO)/p-BST films on the substrate, showing that the n-AO/ZnO films/p-BST TE generator provide much photocurrent than that for AO/ZnO superlattice structures.

6. Maximum power characteristics of 100-nm-thick n-BT/p-BST film-based TE generator

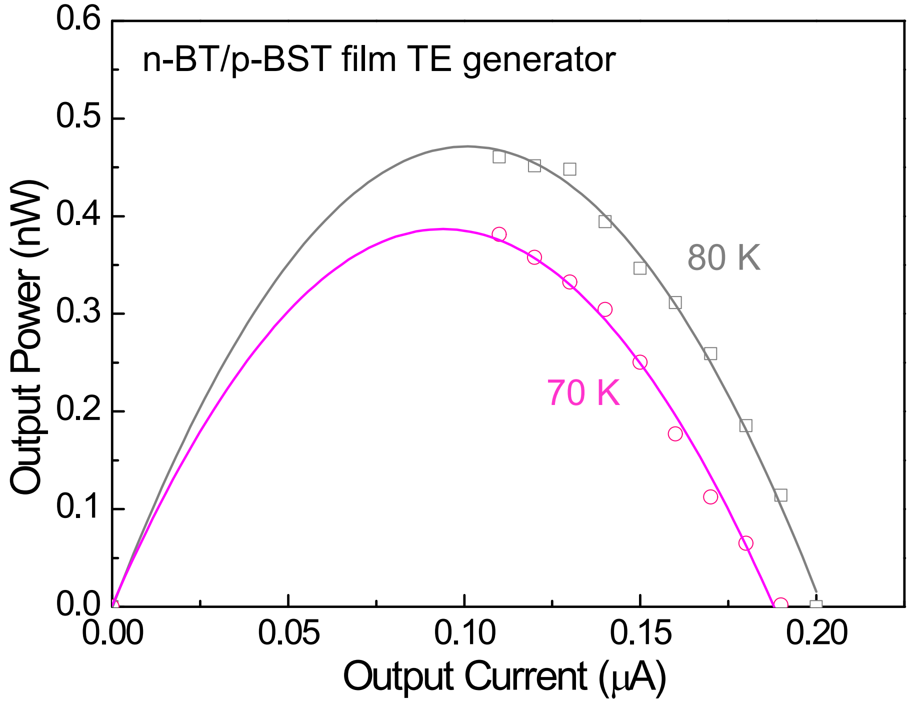

Fig. S5 Output power characteristics of 100-nm-thick n-BT/p-BST film-based TE energy generator, which also composed of four couples of p/n junction legs, at temperature differences of 70 and 80 K between the hot and cold legs in TE generator. The n-BT/p-BST TE generator was annealed at temperature of 200 ℃ under Ar ambient prior to the measurement.

References

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