Electronic supplementary information (ESI)

Layer dependence of out-of-plane electrical conductivity and Seebeck coefficient in continuous mono- to multilayer MoS_2 films

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A. Growth of the monolayer and multilayer MoS_2

The continuous and large-area ML MoS_2 films were synthesized on 300 nm-thick SiO_2/Si substrates using metal-organic chemical vapor deposition (MOCVD). A hot-wall furnace was used to synthesize the films, in which molybdenum hexacarbonyl ($Mo(CO)_6$, MHC), diethyl sulfide ($(C_2H_5)_2S$, DES), argon (Ar), and hydrogen (H_2) were used as chemical precursors to Mo, S, carrier gas, and reduction gas, respectively. The detailed process can be found in the previous report.[1] The continuous and large-area ML MoS_2 was successfully obtained at the 600°C (for 8 hr) temperature with Ar (30 cm^3/min), H_2 (5 cm^3/min), and DES (1 cm^3/min) flows of 60 Torr. Specifically, the MHC flows freely. The 300 nm-thick SiO_2/Si substrates were horizontally situated at the center of the reaction chamber. We first deposited MoO_3 thin films with 99.9% purity (iTASCO) and approximately 5 nm thickness approximately using an e-beam evaporator (Korea Vacuum Tech Co. Ltd.) to grow large-area MTL MoS_2 films. We used a simple sulfurization procedure with H_2 and N_2 gases in a low-pressure chemical vapor deposition (CVD) system.[2] The temperature in the CVD furnace was first raised to 900 °C and maintained for 40 min under H_2 (100 cm^3/min) and N_2 (500 cm^3/min) flow with 0.8 Torr to sulfurize the MoO_3 thin film. Thereafter, sublimation of the sulfur powder (99.998%, Sigma-Aldrich) was initiated in the upstream heating zone at 200 °C. This process was repeated for 30 min to replace O_2 with sulfur in the precursor thin films successfully. The MOCVD-grown ML MoS_2 film was characterized by optical microscopy (OM), Raman, and photoluminescence (PL) spectroscopy. Furthermore, the cross-sectional TEM analysis was performed to verify the morphological features of the ML, BL, and MTL MoS_2. Moreover, the thickness of the MTL MoS_2 layers was investigated by atomic force microscopy (AFM).

B. Sample preparation for evaluating out-of-plane Seebeck coefficient of MoS_2 films

The detailed process can be found previous report.[1] The continuous and large-area ML The large-area ML MoS_2 film was transferred on the Cu thin film/300-nm-thick SiO_2/Si substrate by conventional poly (methyl methacrylate) (PMMA)-assisted wet chemical etching method to measure the out-of-plane Seebeck coefficient.[3, 4] To be more specific, in the case of the ML MoS_2, a thin layer of PMMA (950 K A4) was spin-coated on the as-grown ML MoS_2 film grown on the SiO_2/Si substrate (Fig. 1c); the sample was placed on a hot plate at 120 °C for 2 min. The sample was floated in 5% hydrofluoric (HF) acid for 1 min, in which the Si substrate sank owing to SiO_2 etching, leaving the PMMA/MoS_2 layers to float on top of the HF solution. The PMMA-coated ML MoS_2 film was washed with de-ionized water, transferred to target Cu/SiO_2/Si substrates for measuring the out-of-plane Seebeck coefficients, and dried in ambient conditions. Subsequently, we conducted the O_2 plasma treatment using a plasma surface treatment system (CUTE, Femto Science Inc.) for the Cu/SiO_2/Si substrates during 1 min, which leads to better adhesion between Cu and MoS_2 layers. The transferred ML MoS_2 film on the target substrate (Cu/SiO_2/Si substrate) was annealed at 250 °C for 2 h for better adhesion and the polymer residue removal after removing the PMMA layer using warm acetone. Additionally, Cu metal film was deposited on the transferred ML MoS_2/Cu/SiO_2/Si substrates by radio-frequency (RF) sputtering at room temperature to measure the out-of-plane Seebeck coefficient of the sample using Cu-sandwiched structure; it was then covered with a 200-nm-thick Cu layer using the RF sputtering in an ultrahigh vacuum (UHV). The same method was used for the BL and MTL MoS_2 films. Particularly, the BL MoS_2 was prepared from two MOCVD-grown ML MoS_2 films using the above-mentioned transfer method. Furthermore, cross-section TEM specimens were prepared using the Cu/MoS_2/Cu/SiO_2/Si samples (ML, BL, and MTL MoS_2) with a focus ion-beam (FIB) milling technique (Fig. 1f, Fig. 3a, and Fig. 3b). The thickness of Cu thin films

was ~200 nm. The Cu-sandwiched structures have the advantage of preserving target MoS_2 films during the FIB milling process and clearly observing their morphological features.

C. Measurement setup for evaluating TE properties

We measured the out-of-plane Seebeck coefficients ($S_{\perp}$) of the large-area ML, BL, and MTL MoS_2 films using the Cu-sandwiched structure. Further details of the Seebeck coefficient measurement can be found in our previous works.[5-7] The $Cu/MoS_2/Cu/SiO_2/Si$ (hereafter called $Cu/MoS_2/Cu$) samples were first held between AlN holders, and then a temperature difference was applied across the samples using the micro-Peltier device. The temperature difference was measured using two T-type thermocouples. To minimize the substrate effect (SiO_2/Si substrate) when measuring the $S_{\perp}$, we measured the out-of-plane temperature difference ($\Delta T_{\perp}$) of the $Cu/MoS_2/Cu$ structure under the steady-state condition. The out-of-plane thermoelectric Seebeck voltages were measured by two shielded tungsten needles between the upper and lower Cu thin films. Simultaneously, the electrical conductivity of samples was measured by the two-probe method.

D. Theoretical calculations

The calculations were performed using the ab-initio total-energy and molecular-dynamics program Vienna ab-initio simulation program (VASP) developed at the Institute für Materialphysik of the Universität Wien using the projector-augmented-wave (PAW) approach.[8] Generalized gradient approximation (GGA)[9] was employed for the exchange-correlation energy functional. Moreover, the cutoff energy of 400 eV was used for a plane-wave basis set. The maximum remaining force on each atom was less than ~0.015 eV/Å for structural relaxation. The in-plane lattice parameters of the supercells along the MoS_2/Mg interface planes were fixed to the experimentally determined Mg lattice parameter[10] of $a =$ 3.2028 Å; the supercells were relaxed along the out-of-plane direction, perpendicular to the interface. The Monkhorst-Pack scheme was used to sample the Brillouin zone. The k-point mesh used for MoS_2/Mg was 22 × 22 × 4, 22 × 22 × 3, and 22 × 22 × 2 for the structural relaxation of one, two, and five MoS_2 layers, respectively. The out-of-plane Seebeck tensor component, S_{zz} (i.e., $S_{\perp}$), was calculated using the BoltzTraP code.[11] The mesh for the Seebeck tensor calculations of one, two, and five MoS_2 layers was 48 × 48 × 9, 48 × 48 × 6, and 48 × 48 × 6, respectively.

E. Material parameters for COMSOL calculation

Material	Density (kg/m^3)	Heat capacity at constant pressure (Cp, J/(kg.K))	Thermal conductivity (W/m·K)
Cu	8960	384.80	392.8
MoS_2	5060	397.83	34.5 (∥)/0.3 (⊥)

*Interface thermal conductance (ITC) between Cu and MoS_2: ~2×10^{-9} m^2K/W

F. COMSOL calculation results for Cu/ML MoS_2/Cu

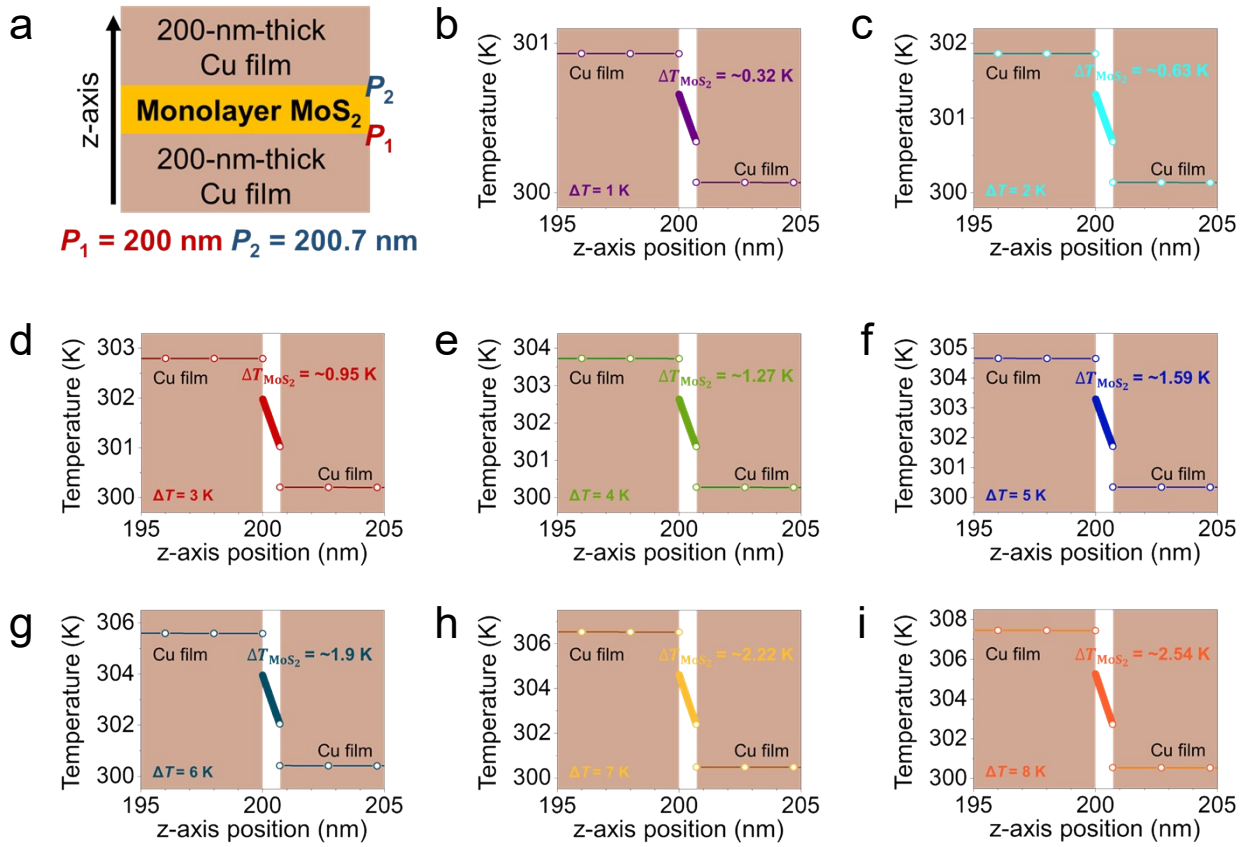

Figure S1. Calculated temperature distribution along the out-of-plane direction (z-axis) in Cu/ML MoS_2/Cu structure.

G. COMSOL calculation results for Cu/BL MoS_2/Cu

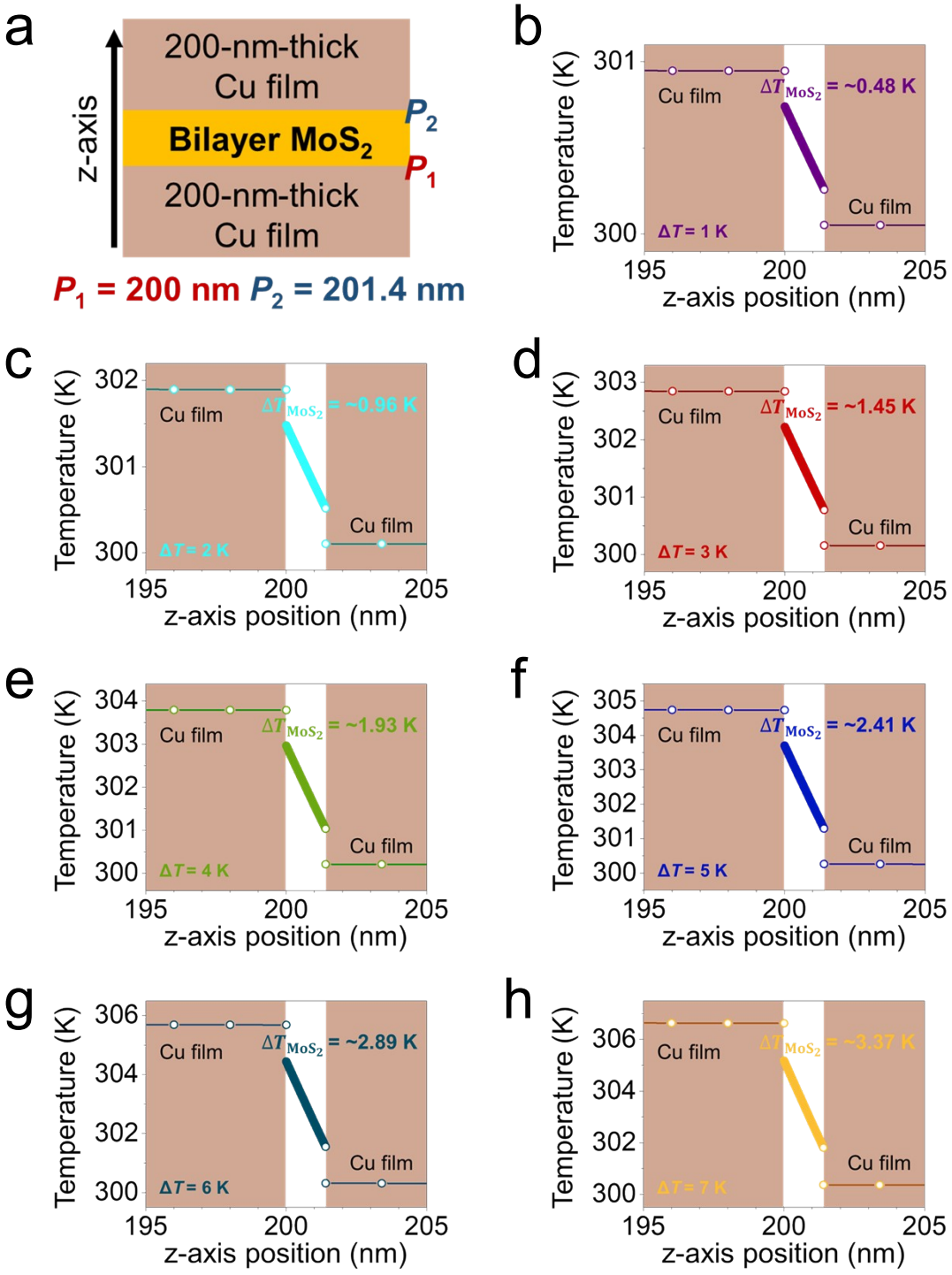

Figure S2. Calculated temperature distribution along the out-of-plane direction (z-axis) in Cu/BL MoS_2/Cu structure.

H. COMSOL calculation results for Cu/MTL MoS_2/Cu

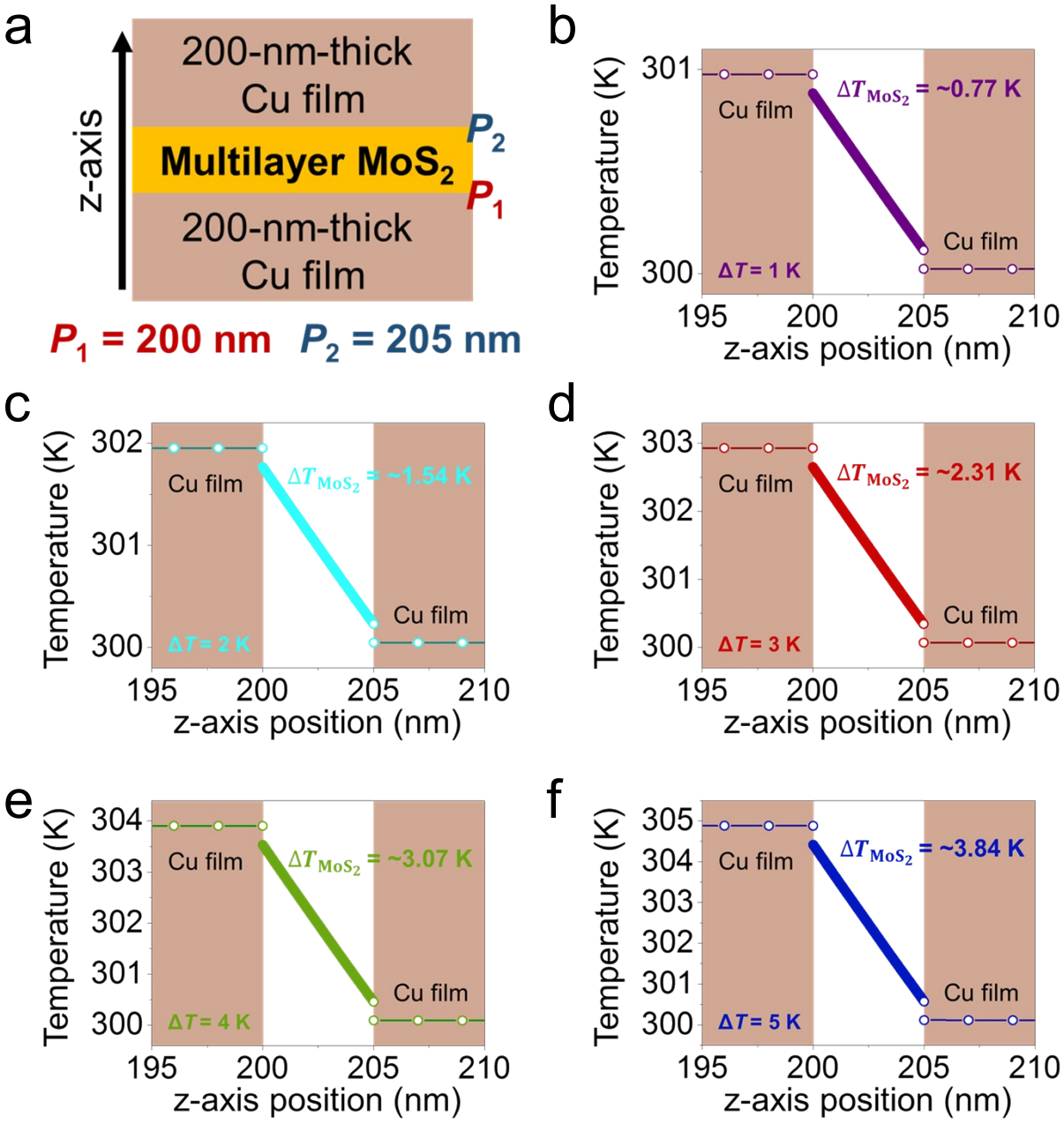

Figure S3. Calculated temperature distribution along the out-of-plane direction (z-axis) in Cu/MTL MoS_2/Cu structure.

I. Band structures of ML and BL MoS_2 system

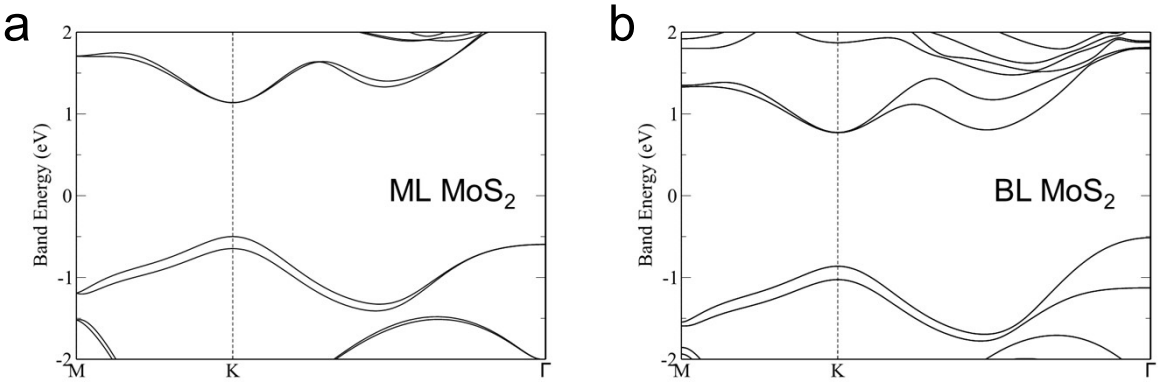

Figure S4. Calculated band structures for (a) ML MoS_2 and (b) BL MoS_2

J. Thickness dependence of the out-of-plane Seebeck voltage

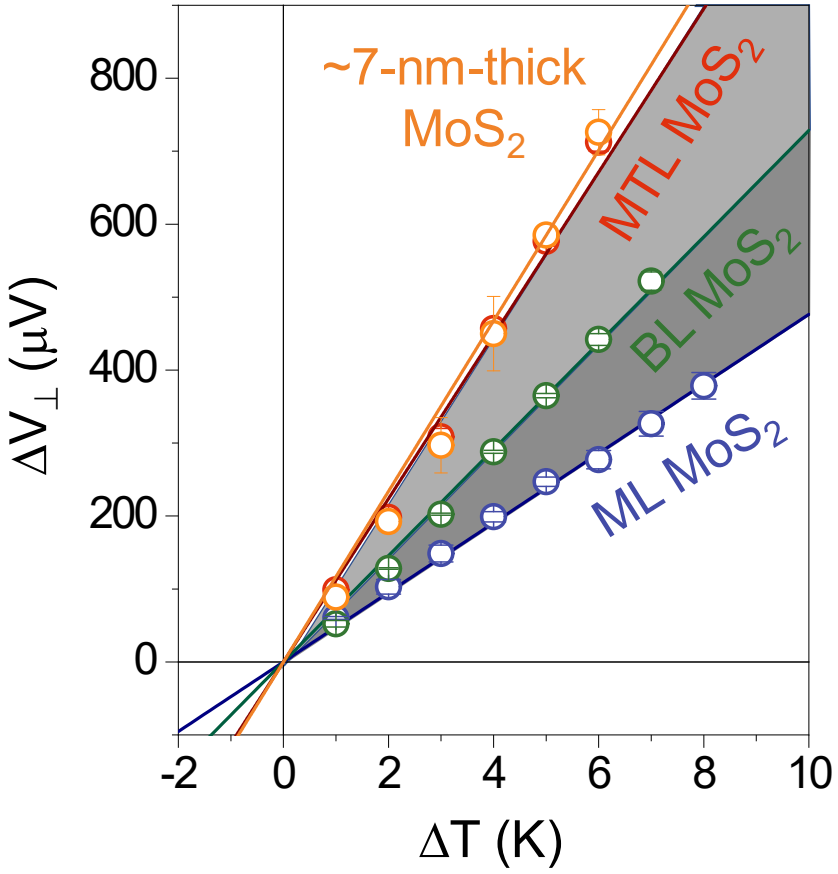

Figure S5. The measured out-of-plane Seebeck voltage difference of ML (~0.7 nm), BL (~1.4 nm), MTL (~4.9 nm), and ~7-nm-thick MoS_2, respectively. The results of ~7-nm-thick MoS_2 is taken from our previous work.[5]

K. Depth-profiling analyses of the Cu/MTL MoS_2/Cu structure

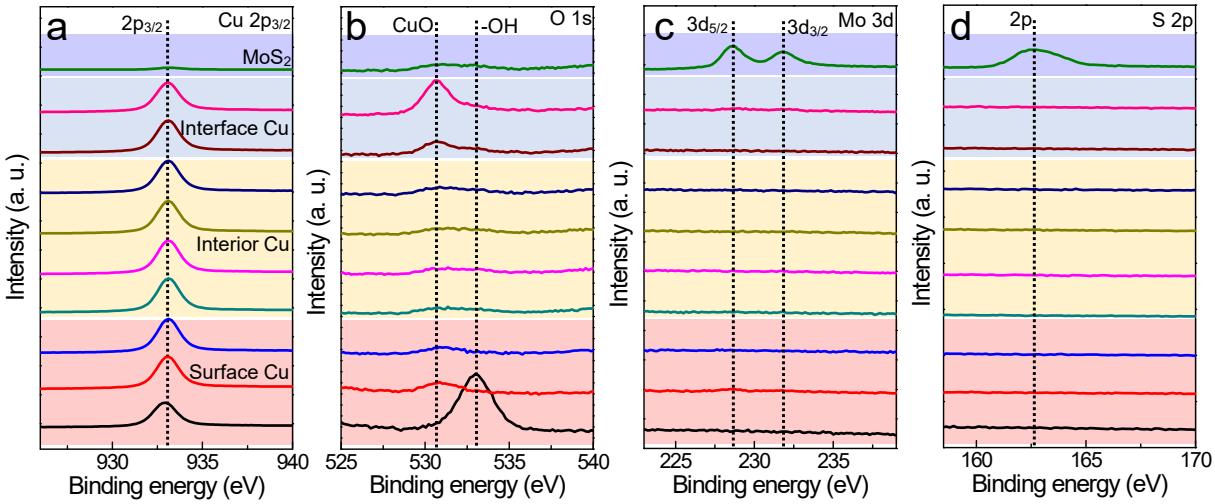

Figure S6. (a)-(d) XPS spectra of the Cu $2p_{3/2}$, O 1s, Mo 3d, and S 2p core levels dependent on etching times, respectively. From these observations, the O 1s peak was found at the surface and interface Cu whereas that peak could not be observed on the interior Cu. It indicates the formation of CuO on the interface region (Cu/MoS_2) caused by wet-transfer process including oxygen (O_2) plasma treatment.

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